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Reactions of Radicals. Part I. Use of Hydrogen Isotopes in Polymer Chemistry. Part II. Hydrogen Atom Reactions in Solution.

Richard Wayne Henderson
Louisiana State University and Agricultural & Mechanical College

REACTIONS OF RADICALS

PART I. USE OF HYDROGEN ISOTOPES IN POLYMER CHEMISTRY

PART II. HYDROGEN ATOM REACTIONS IN SOLUTION

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ABSTRACT

The dissertation is divided into two parts.

Part I. Use of Hydrogen Isotopes in Polymer Chemistry.

The hydrogen secondary kinetic isotope effects in the polymerization of styrene were measured. Through combination of the deuterium and tritium effects it was possible to calculate the isotope effects for all of the various types of hydrogens in the transition state, including those in the polystyryl radical and those in the styrene monomer under attack. The isotope effects for side-chain labeled styrenes appear to have a direct bearing on the interpretation of the isotope effects observed in [2 + 2] cycloadditions, and are discussed in that context. In an extension of these tracer studies to the styrene-maleic anhydride copolymerization system, it was found that there is no isotope effect on the cross-propagation step in which a copolymeric radical having a terminal anhydride unit attacks styrene or styrene-t. Also, the radical reactivity ratios for the comonomers styrene-maleic anhydride were determined.

Part II. Hydrogen Atom Reactions in Solution.

Photolysis of tert-butyl peroxyformate(BUP), $H\text{-}CO_2\text{-}OC(CH_3)_3$, produces appreciable quantities of hydrogen gas, whereas thermolysis does not. Reactivity data and other considerations suggest that the H_2 arises from the reaction of hydrogen atoms resulting from BUP photolysis. Two different systems, both utilizing photolysis of BUP as a convenient source of H-atoms in solution, were developed to study

the abstraction of hydrogen from organic hydrogen donors QH by H-atoms. In the first system deuterated thiol, a very good deuterium donor, was used as a standard reactant RD. An equation was derived in which the relative rate constant for hydrogen abstraction is proportional to the slope of a plot of $[H_2]/[HD]$ vs. $[QH]/[RD]$. The relative reactivities of various hydrogen donors were measured and compared with the results obtained by other methods. The second system utilizes a competition between benzene and QH for hydrogen atoms; in this case equations derived indicate that the slope of a plot of relative H_2 yield vs. $[QH]/[PhH]$ should be proportional to the rate constant for hydrogen abstraction. The results from this system are in substantial agreement with those from other systems.

Substituted toluenes were used as substrates in a study of the polarity of the H-atom. A rho value of -0.13 was found for hydrogen abstraction from the toluenes; this value indicates that the hydrogen atom, like the methyl and phenyl radicals, is only slightly electrophilic.

PART I. USE OF HYDROGEN ISOTOPES IN POLYMER CHEMISTRY

CHAPTER 1
INTRODUCTION

GENERAL DISCUSSION

There are two types of hydrogen isotope effects. The first, or primary, is associated with reactions in which the bond to an isotope undergoes scission or formation during reaction. The second, or secondary, is associated with reactions in which the isotopic bond does not undergo scission or formation during reaction.[1] Secondary isotope effects are further subdivided into two categories: those of the first kind, in which the isotope is bonded to an atom which changes hybridization during reaction, and those of the second kind, in which the isotope is substituted at a more remote position.[1,2]

Substitution of a deuterium at a carbon that changes from sp^3 to sp^2 hybridization produces a normal secondary kinetic isotope effect of 10-15%. That is, $k_H/k_D \sim 1.1$ per deuterium atom.[3] Substitution of a deuterium at a carbon undergoing a hybridization change in the reverse direction, sp^2 to sp^3, gives an isotope effect in the inverse direction ($k_H/k_D \sim 0.96$).[3-6]

Secondary isotope effects have been correlated with the vibrational frequencies of the initial and transition states for the hydrogen and deuterium compounds.[7] In a formulation that can be more easily related to structure and mechanism, Wolfsberg and Stern[8] have established the connection between changes in force constants at the position of isotopic substitution and isotope effects.

In spite of general agreement on the vibrational origin of these effects, there is considerable disagreement over the interaction mechanism responsible for the changes in vibrational force constants during reaction. Secondary isotope effects have been discussed in terms of various electronic effects: induction, hyperconjugation, rehybridization, and non-bonding interactions.[9] A major difficulty in determining the relative importance of each of these effects arises from the fact that usually more than one effect is acting in a particular system. Streitwieser[3b] ascribes the normal α-effect (k_H/k_D = 1.15) in the solvolysis of cyclopentyl-1-d p-toluenesulfonate to an sp^2-sp^3 hybridization change, in which a tetragonal C-H bending mode is transformed to a relatively looser trigonal C-H out-of-plane bending vibration; however, he has suggested that the usual ~15% decrease in solvolysis rate accompanying α-deuterium substitution would be even larger except for an opposing inductive effect.[10]

Bartell[11] has found α- and β-effects can be rationalized in terms of non-bonded interactions, although he has noted that it is impossible to separate completely steric and other electronic effects.[12] It appears, however, that a steric effect is likely to be appreciable only in the case of severe overcrowding.[6,13]

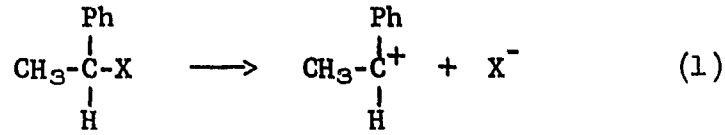
As is true in the case of α-effects, there is no universal agreement on the origin of β-effects. Steric arguments have been invoked,[11,12,14] but the importance of this effect is probably minimal in most systems.[15] The majority of data are best explained by a model involving hyperconjugation between the developing p-orbital and the β-C-H(D) orbital, and induction.[13,15-17] The

latter effect is relatively smaller and apparently works in an opposite direction to hyperconjugation.[15,18-19] For example, Shiner and Humphrey[15] have shown that β-effects are slightly inverse in situations in which hyperconjugation is stereoelectronically prohibited and normal where hyperconjugation is allowed. It is difficult to separate quantitatively the various contributions to α- and β-deuterium isotope effects. Ultimately, though, these forces manifest themselves in vibrational changes, or more fundamentally, in free energy changes.

It has been found that α-effects are generally similar in radical and ionic reactions,[2,20] indicating that the rehybridization effect is dominant, and that development of charge, a second order effect, is relatively unimportant.[20] Thus the changes in α-carbon-hydrogen vibrational frequencies in going from the ground state to the activated complex are similar for ionic and radical reactions. On the other hand, β-effects arise from both hyperconjugative and inductive forces, and since these two factors exert opposing influences on the direction of k_H/k_D,[2,19] β-effects in radical reactions do not always parallel those observed in ionic reactions.

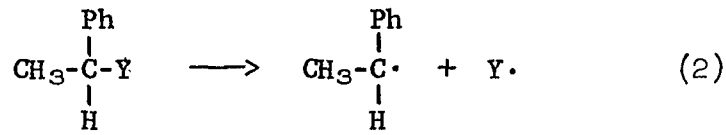
SECONDARY EFFECTS FOR sp^3 TO sp^2 TRANSITIONS

The deuterium kinetic isotope effects in the formation of the 1-phenylethyl moiety by unimolecular heterolysis[20b] (eq 1) and homolysis[20a] (eq 2) are illustrative of the values generally observed. There is a normal α-effect of 14% in both dissociations. The β-effects for heterolytic and homolytic cleavage are about 7%



(1)

X = a halide

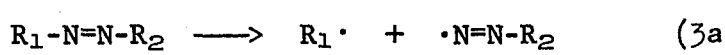


(2)

Y = -N=N-R

and 2%, respectively. Such a large difference in β-effects would not be expected if steric effects were dominant; rather these data are best rationalized in terms of hyperconjugative interaction with the nascent radical or carbonium ion center. There is much less demand for such stabilization in the radical, and the decreased contribution of hyperconjugation is reflected by the smaller β-effect.

Secondary kinetic isotope effects in ionic reactions have been studied extensively,[21] whereas relatively few investigations have been made in radical systems. Isotope effects in the homolysis of various azo compounds have been studied in order to determine whether the two C-N bonds rupture stepwise or simultaneously (see Table I);[20,22] that is, whether dissociation is best described by eq 3 or 4.



(3a)

(3b)

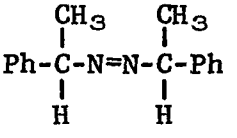
Table I. Secondary Deuterium Isotope Effects in the Decomposition of Various Azo Compounds

Compound	Temperature, °C	k_H/k_D [a,b]	Reference
$Ph-\overset{CH_3}{\underset{}{CD}}-N=N-\overset{CH_3}{\underset{}{CD}}-Ph$	105	1.13	c
$PhCH_2-\overset{Ph}{\underset{}{CD}}-N=N-\overset{Ph}{\underset{}{CD}}-CH_2Ph$	106.5	1.10	d
$Ph-\overset{CH_3}{\underset{}{CD}}-N=N-\overset{CH_3}{\underset{}{CH}}-CH_3$	143.2	1.15	e
$Ph-\overset{CH_3}{\underset{}{CH}}-N=N-\overset{CH_3}{\underset{}{CD}}-CH_3$	143.2	1.04	e
$Ph-\overset{CH_3}{\underset{}{CD}}-N=N-CH_3$	161.0	1.13	f
$Ph-\overset{CH_3}{\underset{}{CH}}-N=N-CD_3$	161.0	0.97	f
$Ph-\overset{CD_3}{\underset{}{CH}}-N=N-\overset{CD_3}{\underset{}{CH}}-Ph$	105	1.02	g
$(CD_3)_2\overset{CN}{\underset{}{C}}-N=N-\overset{CN}{\underset{}{C}}(CD_3)$	70	1.02	h

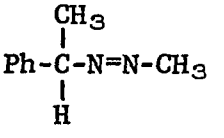
[a] k_D refers to the compound shown; k_H refers to the unlabeled azo compound. [b] On a per deuterium basis. [c] S. Seltzer, J. Amer. Chem. Soc., 83, 2625 (1961). [d] S. Scheppele and S. Seltzer, ibid., 90, 358 (1968). [e] S. Seltzer, ibid., 85, 14 (1963). [f] S. Seltzer and F. Dunne, ibid., 87, 2628 (1965). [g] S. Seltzer and E. Hamilton, Jr., ibid., 88, 3775 (1966). [h] S. Rummel, H. Hubner and P. Krumbiegel, Z. Chem., 7, 351(1967).

$$R_1\text{-}N{=}N\text{-}R_2 \longrightarrow R_1\cdot + N_2 + R_2\cdot \qquad (4)$$

α-Effects of about 15% per deuterium would be expected for reactions in which a C-N bond is undergoing scission; α-effects smaller than 15% in a unimolecular decomposition are indicative of less breaking of that bond in the transition state. On this basis, Seltzer was able to classify azo decompositions in terms of one-step or two-step mechanisms.[22] Thus there is a normal α-effect of 13% per deuterium in the decomposition of azobis-α-phenylethane (I), indicating that the two C-N bonds are breaking simultaneously.[20] α-Phenylethylazomethane (II) apparently undergoes one-bond scission, since the α-effect is 13% normal for the phenylethyl moiety, but an



I

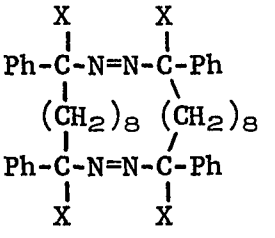


II

inverse effect of 1% results for each deuterium substituted in the methyl group.[23] Available evidence indicates that the activation energy for two-bond scission is lowered, relative to that for one-bond scission, as the degree of resonance stabilization of the alkyl fragments attached to the azo group increase. Pryor finds that the rate constant for decomposition of azocumene is independent of solvent viscosity,[24] which indicates that the compound undergoes multi-bond cleavage. Since the cumyl and α-phenylethyl radicals

have the same resonance stabilization energies (within a few kilocalories per mole), the results from isotope effect and viscosity tests are in harmony.

On the basis of the isotope effect (k_H/k_D = 1.20 for four deuterium atoms) Seltzer[22] concludes that the two azo groups in III act independently, since a 12% effect per deuterium would be expected

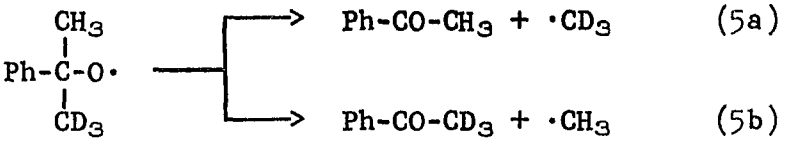


III a, X = H
b, X = D

if concerted loss of both nitrogens was occurring. This conclusion is based on the reasonable assumptions that the two C-N bonds in one azo linkage undergo simultaneous scission and that this scission leads to an α-effect similar to that found in comparable non-cyclic azo compounds.

Thus a change from sp^3 to sp^2 hybridization in azo decompositions is accompanied by a normal α-effect of about 12% per deuterium. β-Effects are much smaller, varying from ~1% inverse to ~2% normal.

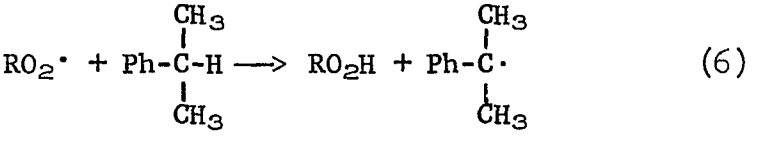
Zavitsas and Seltzer[10b] have reported that at 75°, k_H/k_D = 1.12 per deuterium for the following reaction:



$$\mathrm{Ph\text{-}C(CH_3)(CD_3)\text{-}O\cdot} \longrightarrow \mathrm{Ph\text{-}CO\text{-}CH_3} + \cdot\mathrm{CD_3} \qquad (5a)$$

$$\mathrm{Ph\text{-}C(CH_3)(CD_3)\text{-}O\cdot} \longrightarrow \mathrm{Ph\text{-}CO\text{-}CD_3} + \cdot\mathrm{CH_3} \qquad (5b)$$

Boozer et al.[25] have purportedly isolated the following step in the autoxidation of cumene, and have reported that the rate is



$$\mathrm{RO_2\cdot} + \mathrm{Ph\text{-}C(CH_3)_2\text{-}H} \longrightarrow \mathrm{RO_2H} + \mathrm{Ph\text{-}C(CH_3)_2\cdot} \qquad (6)$$

decreased about 10% for each deuterium substituted in a methyl group. This value is abnormally large for a β-effect, and it is possible that the isotope effect is rendered meaningless by complicating side reactions.[26]

A slightly inverse α-effect (k_H/k_D = 0.99 per deuterium at 366°) on the pyrolysis of dimethylmercury was observed by Weston and Seltzer.[27] The authors attribute this unexpected result to a large increase in C-H stretching frequencies in the transition state, and suggest that the usually dominant change in the out-of-plane bending frequency is negligible in the pyrolysis of dimethylmercury. However, this anomaly may be explained by the thermal nonequilibrium conditions present at the low pressure used (600 mm Hg). For example, both the magnitude and direction of the isotope effect on the isomerization of CH_3NC to CH_3CN are pressure dependent; k_H/k_D = 0.9 at 600 mm Hg and 1.07 at the high pressure limit.[28]

Koenig[29] has studied the deuterium isotope effects in the decomposition of various peresters (see Table II). Except in the case of t-butyl peracetate and t-butyl p-methoxyphenylperacetate, the value of an α-effect is only 5-6%. Even so, Koenig concludes that bond scission is synchronous, since these values are too large to attribute to β-effects, and also since $k_H/k_D = 1.0$ for homolysis of peroxy compounds known to undergo single bond cleavage. The results from Pryor's viscosity test indicate that t-butyl peracetate and t-butyl p-methoxyphenylperacetate are multi- and single-bond initiators, respectively,[24] in agreement with the conclusions of Koenig[29] (based on isotope effects) and Bartlett[30] (based on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values). Pryor finds that the rate constants for decomposition of t-butyl phenylperacetate and t-butyl p-nitrophenylperacetate are viscosity dependent, indicative of single-bond homolysis;[24] the conclusion of Koenig,[29] Bartlett[30] and Neuman[31] (based on the pressure dependence of the rate constants) is that both of these compounds decompose by a concerted mechanism. The reason for this discrepancy is not clear.[32]

The mode of decomposition of acetyl peroxide has generated a great deal of controversy. There is uncertainty as to whether thermolysis proceeds by single O-O bond cleavage, by concerted two-bond cleavage, or by concerted three-bond cleavage. Early work involving isotope and scavenger studies indicated that acetyl peroxide was a multi-bond initiator.[33] However, Taylor and Martin[34] reversed this when they observed ^{18}O scrambling between the carbonyl and peroxidic oxygens in recovered peroxide; this result implies

Table II. Secondary Deuterium Isotope Effects in the Decomposition of Various Peresters

R in R-CO_2-OBu-t	Temperature, °C	k_H/k_D [a,b]	Reference
CD_3-	130.1	1.00	c
$(CD_3)_3C$-	73.9	1.02	d
$(CD_3)_2\overset{Ph}{\overset{|}{C}}$-	60.6	1.02	d
Ph-$\overset{CH_3}{\overset{|}{C}}$D-	74.0	1.05	d
Ph-$\overset{CD_3}{\overset{|}{C}}$H-	73.9	1.02	d
Ph-CD_2-	85.0	1.06	d
p-NO_2-C_6H_4-CD_2-	85.0	1.05	c
p-MeO-C_6H_4-CD_2-	60.4	1.03	c

[a] k_D refers to the perester shown; k_H refers to unlabeled perester. [b] On a per deuterium basis. [c] T. Koenig, J. Huntington and R. Cruthoff, J. Amer. Chem. Soc., 92, 5413 (1970). [d] T. Koenig and R. Wolf, ibid., 91, 2574 (1969).

that acetoxy radicals have a finite, though tenuous, existence. Koenig and Cruthoff[35] found that the rate of decomposition of acetyl peroxide is virtually unaffected by deuterium substitution (k_H/k_D = 1.01), which also indicates that there is little or no methyl radical character in the rate-determining transition state. Pryor's results also support a one-bond scission mechanism, since the observed rate constant for decomposition of acetyl peroxide is viscosity dependent.[24]

SECONDARY EFFECTS FOR sp^2 TO sp^3 TRANSITIONS

The secondary kinetic isotope effects in the addition of various radicals to deuterated olefins are shown in Table III. Generally, a small inverse effect of about 3-5% is observed for each deuterium substituted at a carbon undergoing on sp^2 to sp^3 hybridization change. Isotope effects in the homolytic substitution of aromatic compounds have been studied,[36] but it is not possible to draw unambiguous conclusions from the results. Normal isotope effects are usually observed; for example, k_H/k_D = 1.14 for addition of O (^3P) to benzene and benzene-$\underline{d}_6$.[37]

A number of studies have been made of the isotope effects in the polymerization of styrene.[4d,38-43] Much of the interest in this area is due to the fact that even rigorously purified styrene is able to induce the formation of free radicals at a reproducible rate at temperatures far too low for unimolecular bond homolysis.[44] The mechanism of thermal polymerization has remained an enigma for several decades.[45] A summary of the isotope effects on k_p, the

Table III. Secondary Deuterium Isotope Effects in Radical Additions to Olefins

Radical	Olefin	Temperature, °C	k_H/k_D [a,b]	Reference
H·	CD_2=CD-CD_3	25	0.97	c
CH_3·	CD_2=CD_2	65	0.97	d
	CD_2=CH-CH_3	65	0.95	d
	CD_2=CD-CD_3	65	0.93	d
	CD_2=CD-CD=CD_2	65	0.91	d
	CD_2=CD-Ph	50	0.96	e
CF_3·	CD_2=CD_2	65	0.96	d
	CD_2=CH-CH_3	65	0.96	d
	CD_2=CD-CD_3	65	0.96	d
	CD_2=CD-CD=CD_2	65	0.93	d
	CD_2=CD-Ph	65	0.95	d

[a] k_D refers to addition to the olefin shown; k_H refers to addition to unlabeled olefin. [b] On a per deuterium basis; it is assumed that only the deuteriums substituted at a carbon undergoing an sp^2 to sp^3 hybridization change contribute to the isotope effect. [c] M. Takahasi and R. J. Cvetanovic, Can. J. Chem., 40, 1037 (1962). [d] M. Feld, A. Stefani and M. Szwarc, J. Amer. Chem. Soc., 84, 4451 (1962). [e] M. Matsuoka and M. Szwarc, ibid., 83, 1260 (1961).

propagation rate constant, in the radical polymerization of various deuteriostyrenes is given in Table IV. The observed isotope effects consist of two components: one arising from the deuteration in the radical and the other arising from the deuterated monomer.

It should be mentioned that secondary isotope effects have been observed in mechanistic studies of cycloadditions and retro-processes. They give isotope effects generally in accord with the rules outlined above, but the radical nature of these reactions is speculative.[46]

THE PRESENT CONTRIBUTION

In order to expand knowledge in the field of isotope effects in radical reactions, we initiated a program of study to determine accurately the contribution of each deuterium to the observed isotope effects in the polymerization of labeled styrenes. A convenient technique utilizing tritium-labeled styrenes at tracer levels was employed, and values of k_H/k_T (see eq 7) were obtained for attack of the polystyryl radical on styrene *vs.* styrene-*t* for

$$M_n\cdot + \text{styrene} \xrightarrow{k_H} M_{n+1}\cdot \qquad (7a)$$

$$M_n\cdot + \text{styrene-}t \xrightarrow{k_T} M_{n+1}\cdot \qquad (7b)$$

styrene-α-*t*, -β-*t* and -*p*-*t*. These isotope effects were transformed into k_H/k_D values *via* the Swain equation;[47] it was then possible to calculate the effect of each deuterium, including those

Table IV. Secondary Deuterium Isotope Effects on the Propagation Rate Constant, k_p, for Various Deuteriostyrenes

Reactants		k_H/k_D [a]			
Radical	Monomer	Ref. b	Ref. c	Ref. d	Ref. e
$M_n-CH_2-\overset{Ph}{\underset{}{C}}D\cdot$	$CH_2=\overset{Ph}{\underset{}{C}}D$	0.91	0.90	-	0.86
$M_n-CD_2-\overset{Ph}{\underset{}{C}}H\cdot$	$CD_2=\overset{Ph}{\underset{}{C}}H$	0.88	0.87	1.00	0.81
$M_n-CH_2-\overset{C_6D_5}{\underset{}{C}}H\cdot$	$CH_2=\overset{C_6D_5}{\underset{}{C}}H$	0.83	1.00[f]	-	0.96[g]
$M_n-CH_2-\overset{Ph\text{-}p\text{-}D}{\underset{}{C}}H\cdot$	$CH_2=\overset{Ph\text{-}p\text{-}D}{\underset{}{C}}H$	-	1.00	-	-

[a] k_H refers to attack on unlabeled monomer by an unlabeled radical; k_D refers to the reaction shown. [b]W. A. Pryor, R. W. Henderson, R. A. Patsiga and N. Carroll, J. Amer. Chem. Soc., 88, 1199 (1966). [c]K. Kirchner, Makromol. Chem., 96, 179 (1966). [d]G. S. Hammond and K. Kopecky, J. Polym. Sci., 60, 554 (1962). [e]K. Kopecky and S. Evani, Can. J. Chem., 47, 4049 (1969). [f]Styrene-o,o,p-d_3. [g]Styrene-o,o-d_2.

in the polystyryl radical and those in the monomer under attack.

The second phase of our program involved extension of these tracer studies to copolymerizations. We measured the isotope effect on the cross-propagation step (eq 8), in which the growing polymeric radical having a maleic anhydride(MA) terminal unit adds to styrene (S) or styrene-t(S*). Tritium secondary isotope effects in styrene

$$\sim MA\cdot + S \xrightarrow{k_H} \sim MA\text{-}S\cdot \qquad (8a)$$

$$\sim MA\cdot + S^* \xrightarrow{k_T} \sim MA\text{-}S^{*}\cdot \qquad (8b)$$

polymerizations were found to be rather small; thus, labeled styrenes could be used in very sensitive determinations of copolymer compositions. The reactivity ratios for the styrene-maleic anhydride system were determined as an illustrative example of the usefulness of this method.

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CHAPTER 2

EXPERIMENTAL SECTION

PREPARATIONS AND PURIFICATIONS

α-Bromostyrene.[1,2] Gaseous hydrogen bromide was generated by the dropwise addition of phosphorus tribromide to water. The gas was dried over a train of $CaCl_2$ and P_2O_5, and bubbled through an ice cold solution of phenylacetylene (170 ml, 1.55 moles) in 100 ml of hexane over a period of 4 hr. The solvent was removed, and the residue was distilled through a short, packed column to give recovered phenylacetylene (20 g, 0.19 mole, bp 28-29° at 8 mm), and 180 g of an oil (bp 24-60° at 0.5 mm). A solution of this oil and 90 ml of saturated alcoholic potassium hydroxide was allowed to stand for 2 days at -15°. After separation of layers, the organic phase was washed, dried and distilled to give 153 g of an oil, bp 40-55° (0.7 mm). This oil was mixed with 320 ml of water, 36 g of sodium carbonate, 46 g of hydroxylamine hydrochloride, and 9 ml of ethanol, and this mixture was allowed to stand for 2 days at -15°. The organic phase was washed, dried and distilled to give α-bromostyrene (139 g, 55% yield, bp 41-42° at 0.7 mm). In some experiments α-bromostyrene purchased from the Chemical Intermediates and Research Co. (P.O. Box 146, Cuyahoga Falls, Ohio) was used; it had essentially the same degree of purity as the material synthesized above, although the impurities were not identical.

Analysis by gas phase chromatography (gpc) indicated a composition of 95% α-bromostyrene, 4% trans-β-bromostyrene and about 1%

of an unidentified third material. The nuclear magnetic resonance (nmr) spectrum taken with a Varian A-60A instrument (29% in carbon tetrachloride; TMS internal standard) showed broad absorption from 7.0 to 7.6 ppm due to the aromatic protons, a pair of doublets with a splitting of 2 cps centered at 5.62 and 5.90 ppm due to the two β protons, and a peak from an impurity at 4.1 ppm (not β-bromostyrene). No styrene impurity was present. The infrared spectrum confirmed the identification, showing strong peaks at 3.28, 5.95, 6.20, 6.71, 6.91, 7.82, 8.25, 9.45, 9.75, 11.3, 13.0 and 14.3 μ.

Styrene-α-d was synthesized to demonstrate the isotopic purity of the tritiated compounds.[3] A solution of α-bromostyrene (50 g, 0.27 mole) in 100 ml of tetrahydrofuran (THF) was added dropwise to a stirred mixture of magnesium (15.0 g, 0.62 mole) in 25 ml of THF in a flask flushed with dried nitrogen. Mild refluxing was maintained during addition and then for another 30 minutes. The Grignard salt was hydrolyzed with 9 ml of D_2O (99.8%, Nuclear Research Chemicals) in 50 ml of THF, after which the solution was washed with a mixture of 100 ml of water, 50 ml of HCl and 50 ml of ether. The organic layer was separated, the aqueous phase was washed with 30 ml of ether, and the combined organic phases were washed with a saturated sodium chloride solution. Ether was removed under reduced pressure and the styrene distilled, giving 10.3 g (bp 32-33° at 10 mm) of product.

The infrared spectrum of this styrene-α-d agreed with that reported by Kobayashi,[4] showing peaks at 3.41, 4.50 (C-D stretch), 6.20, 6.70, 6.92, 7.12, 8.25, 9.30, 9.75, 11.0, 12.0, 13.0 and

14.5 μ. The spectrum reported by Kobayashi has a peak at 12.4 μ which is missing in our material. The nmr spectrum[5,6] shows a peak at 5.10 ppm and one at 5.63 ppm due to the trans- and cis-β protons, respectively, with a splitting of 2 cps, a peak at about 7.2 ppm due to the aromatic protons, and only low absorption at 6.3 to 6.9 ppm, the region characteristic of an α proton. Integration gives 118:3:24:24 for the areas of the aromatic, α, cis-β, and trans-β protons, respectively, implying that normal styrene is present as an impurity to the extent of about 12%. The small amount of trans-β-bromostyrene present in the α-bromostyrene, the equivalence of the areas of the two β protons, and the 5.0:2.02 ratio of ring to β protons all indicate that no styrene-β-d is produced by this synthesis.

Styrene-α-t was prepared by a procedure similar to that above. α-Bromostyrene (3.0 g, 0.016 mole) in THF(6 ml) was added over 30 minutes to magnesium turnings (0.72 g, 0.03 mole) in THF(6 ml), after which the mixture was stirred for one hour at room temperature. Hydrolysis was accomplished by adding 75 λ H_2O-t (3.75 mCi; Nuclear Research Chemicals) in 0.23 ml of water and 10 ml of THF over 10 min from a dropping funnel. A stream of nitrogen was passed over the reaction mixture until the volume was reduced by one third. Commercial styrene (50 ml) was added, and the solution distilled; the middle fraction was collected at 27° (6 mm). The yield was 20 ml of material with an activity of approximately 3.6×10^6 disintegrations per minute per gram (DPM/g), a 25% yield based in tritium (this calculation allows for a statistical factor of 1/2 in the

hydrolysis step but not for an isotope effect). This material was diluted with 100 ml of styrene and redistilled; the center cut was prepolymerized[7] and redistilled to afford 60 ml of purified monomer.

Permanganate oxidation[8] of a sample of styrene-α-t yielded inactive benzoic acid, which indicates that labeling is not introduced into the ring during the synthesis. One gram of styrene-α-t was added to a solution consisting of 60 ml of water, 4 g of $KMnO_4$, and one ml of 10% sodium hydroxide. The mixture was refluxed for 3 hours, then cooled to room temperature, filtered, acidified with sulfuric acid and refrigerated for one hour at -5°. The acid was collected on a filter and recrystallized from benzene. The count rate for 20.7 mg of this benzoic acid was 47.0 CPM (background = 24.6 CPM). Thus more than 99.9% of the activity in the styrene is removed by the oxidation.

β-Bromostyrene was relatively pure as purchased from Eastman. Recrystallization increased the trans to cis ratio but did not otherwise affect purity. The material used for synthesis was estimated by gpc to be 90% trans. The infrared spectrum supports the analysis, showing major peaks in agreement with those of Yoshino, et al.[6b] The nmr spectrum has areas in the ratio of 5.0:1.0:1.0 for the aromatic, α, and β protons, as expected. α-Bromostyrene definitely is not present.

Styrene-β-d. β-Bromostyrene (5.0 g, 0.027 mole) and ethyl bromide (4.5 g, 0.041 mole) were combined with 15 ml of THF, and added drop-wise over an hour to a stirred mixture of 1.82 g of magnesium (0.078 mole) in 20 ml of THF. The temperature was kept

below 60° during the addition, after which the reaction mixture was allowed to stand at room temperature for an hour. A solution of 10 ml of D_2O in 20 ml of THF was used to hydrolyze the Grignard salt; distillation yielded about one gram of styrene-β-d (bp 27°/5 mm). The nmr of this material showed protons in the ratio of 5.0:1.08:1.09 for the aromatic, α, and β positions, respectively. Therefore styrene-α-d was absent; comparison of the infrared spectra of α- and β-styrene-d confirmed this. There was no absorption band at 3.02μ in the infrared spectrum of the product; thus phenylacetylene, which has a strong band at 3.02μ, was not present as an impurity.

Styrene-β-t. Prior to the addition of water to hydrolyze the Grignard salt, the same procedure was used for preparation of styrene-β-d and -β-t. At this juncture tritiated water replaced the D_2O, and the synthesis continued as follows: a mixture of 40 λ of H_2O-t (2 mCi) and 1.22 ml of water (0.07 mole) was added to 15 ml of THF. The Grignard solution was diluted with 30 ml of THF, and the THF-water mixture was added to it from an addition funnel over a 45 minute period.

Normal styrene (40 ml) was added, the volatile material was removed under reduced pressure, and a 20 ml fraction boiling at 27° (5 mm) was collected; this fraction was combined with another 40 ml of styrene and redistilled (27° at 6 mm) after prepolymerization.[7] The specific activity of this material was 5.4×10^6 DPM/g, a 5% yield based on tritium. Oxidation[8] of styrene-β-t removed 99.8% of the activity.

p-Bromostyrene (Columbia Organic Chemicals) was free of impurities, as shown by gpc and the nmr and infrared spectra.

Styrene-p-t was synthesized by the same procedure as was used to prepare styrene-α-t, except that p-bromostyrene replaced α-bromostyrene in the reaction sequence. Benzoic acid resulting from permanganate oxidation of this material had essentially the same activity (4.33×10^8 DPM/mole) as the styrene-p-t (4.41×10^8 DPM/mole), indicating that only the ring was labeled and also that ring activity was inviolable during side-chain oxidation. This result demonstrated that the lack of activity in the benzoic acid prepared from styrene-α-t and β-t was conclusive evidence that no ring-labeling was present in these two tritiated monomers.

Styrene-o-t. Attempts to prepare styrene-o-t (using o-bromostyrene) were unsuccessful; in each case only inactive material was isolated.

Styrene (Eastman White Label) was distilled, prepolymerized,[7] and redistilled. The prepolymerization and distillation procedure was repeated immediately prior to use.

Maleic Anhydride (Fisher) was recrystallized from chloroform two times, and then dried in a vacuum desiccator.

2,2'-Azo-bis-isobutyronitrile (Eastman White Label) was recrystallized twice from ethanol, and then dried in a vacuum desiccator.

Toluene (Baker) and p-dioxane (Matheson, Coleman and Bell reagent grade) were dried and distilled prior to use.

POLYMERIZATION TECHNIQUES

Polymerizations were conducted in sealed ampoules, and polymers were isolated either by precipitation with methanol or by freeze-drying. In a typical polymerization, a measured amount of a benzene solution of azo-bis-isobutyronitrile (AIBN) was introduced into a 10-ml ampoule, and the benzene was pumped off. The required amount of monomer(s) was added, and the ampoule was attached to a vacuum line. The ampoule was de-aired by three freeze-pump-thaw cycles, sealed off under vacuum, and placed in a constant temperature bath for the appropriate length of time. The reaction mixture was diluted with an equal volume of benzene and then poured into twice its volume of ice cold (-15°) methanol. The polymer was filtered (Whatman No. 2 filter paper) from the precipitation mixture, dissolved in 5 ml of benzene, and freeze-dried.[9] The dry, fluffy polymer was redissolved in 5 ml of benzene, and the freeze-drying procedure was repeated four times. If quantitative transfer of polymer was desired, the entire polymerization solution was washed with benzene into an Erlenmeyer flask, after which freeze-drying was performed in the usual way. It was found that repeated precipitations did not affect the specific activity of the polymer. Styrene-maleic anhydride copolymer was isolated by the procedure outlined above, except that p-dioxane replaced benzene as solvent. Occasionally a small amount of acetone was added to effect complete dissolution of the copolymer.

COUNTING PROCEDURES

An ambient-temperature Beckman LS-250 Liquid Scintillation Spectrometer was used for counting the tritiated samples. In the case of polystyrene the liquid scintillation counting (LSC) solution was toluene containing 1 g/l. of 1,4-bis-2-(4-methyl-5-phenyloxazoyl)-benzene (dimethyl POPOP) and 6 g/l. of 2,5-diphenyloxazole (PPO). The styrene-maleic anhydride copolymers were insoluble in toluene; the LSC solution used for them was p-dioxane containing 0.8 g/l. of dimethyl POPOP, 6 g/l. of PPO, and 80 g/l. of naphthalene. Quenching was monitored by the external standard-channels ratio (ESCR) method, which utilizes a channels ratio of external standard counts in two windows.

After a two-hour dark adaptation period each sample was counted a minimum of five times (approximately 10^6 total counts, a 2 σ error of $\pm$0.2%), and its count rates and ESCR values were averaged. A variety of quenching agents (e.g., benzoic acid, nitromethane, chloroform, polystyrene) gave the same efficiency correction line, and so count efficiency was measured with a set of sealed Packard standards in which nitromethane was present as a quencher. Styrene quenched severely, but its polymer did not. For this reason, styrene was converted as completely as possible to polymer, and the activity of this high-conversion polymer was used as a first approximation to the monomer activity (see Appendix A). This method was considered to be the most direct way of comparing the specific activity of monomer and low-conversion polymer. Standard samples of 15 to 50 mg of polymer in 13 ml of LSC solution were counted, and a correction was made for the small amount of quenching.

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consists of freezing the polymer-benzene solution and then pumping off benzene; as long as the benzene sublimes, the cake remains cold enough to stay solid. Usually 1-2 hours are required.

CHAPTER 3
RESULTS AND DISCUSSION

HYDROGEN ISOTOPE EFFECTS IN STYRENE POLYMERIZATION

Tritiated styrene is present at tracer levels, and therefore the only important reaction which leads to labeled polymer is attack on styrene-t by a polymeric radical which has an unlabeled end unit. It is assumed that the partition

$$M_n\cdot + \text{styrene} \xrightarrow{k_H} M_{n+1}\cdot \qquad (1a)$$

$$M_n\cdot + \text{styrene-t} \xrightarrow{k_T} M_{n+1}\cdot \qquad (1b)$$

is not affected by the presence of a tritiated end monomer unit in the radical. Equation 2 was used to calculate k_H/k_T.[1,2]

$$k_H/k_T = \frac{\ln(1 - f_i)}{\ln(1 - \frac{SAP_i}{SAM} f_i)} \qquad (2)$$

where SAP_i is the specific activity of the polymer at macroscopic conversion fraction f_i and SAM is the specific activity of the monomer. The method used to determine SAM is described in the experimental section and Appendix A (in which a sample calculation is given). Briefly, styrene-t was converted to polymer as quantitatively

as possible, and the polymer was isolated and counted. The value of SAP for this high-conversion polymer was used as a first approximation to SAM, and k_H/k_T was calculated for low conversion runs, using eq 3.

Since kinetic chain lengths are long ($\sim 10^4$), it should be immaterial whether these polymerizations are initiated thermally or with AIBN to attain a particular fraction conversion. Hodnett[2] found this to be true for styrene-$\underline{\beta}$-^{14}C, and we found similar results with tritiated styrene (see Table I), both for low and high conversion runs.

The isotope effects in the polymerization of styrene-$\underline{\alpha}$-$\underline{t}$, -$\underline{\beta}$-$\underline{t}$ and -$\underline{p}$-$\underline{t}$ are shown in Tables II, III, and IV, respectively, and a summary is given in Table V. We find that the isotope effect is 4% normal in the case of styrene-$\underline{\alpha}$-$\underline{t}$, 3% inverse for styrene-$\underline{\beta}$-$\underline{t}$, and that there is no effect in the case of styrene-$\underline{p}$-$\underline{t}$. Table VI shows that the isotope effect for styrene-$\underline{\beta}$-$\underline{t}$ is constant in various media. Previously, values of k_H/k_T of 0.99 for styrene-$\underline{\alpha}$-$\underline{t}$ and 0.93 for styrene-$\underline{\beta}$-$\underline{t}$ were reported;[3] these results were obtained on a liquid scintillation counter operating at only 12% efficiency. The Beckman LS-250 liquid scintillation counter employed in the present study operated at an efficiency of about 50%, and it appears that machine inefficiency in the former work is the source of the discrepancy. It should be pointed out that in the previous work[3] the styrene-$\underline{\beta}$-$\underline{t}$ isotope effect became more inverse with increasing temperature, contrary both to simple theory and to our present results.

Table I. Effect of Polymerization Conditions on the Specific Activity of Polymers(SAP)

Monomer	Temperature, ^{o}C	[AIBN] $x10^{3}$	Conversion, %	SAP $x10^{-6}$[a]
		Low Conversion Runs		
Styrene-β-t	60	-	5.9	5.49
Styrene-β-t	60	6.15	7.5	5.50
Styrene-p-t	60	-	3.6	8.47
Styrene-p-t	60	3.05	8.9	8.41
		High Conversion Runs		
Styrene-β-t	60	1.23	92.6	5.38
Styrene-β-t	100	-	89.9	5.33

[a]In disintegrations per minute per gram(DPM/g).

Table II. Isotope Effects for Styrene-α-t at 60 and 100°

No.	Temperature, °C	[AIBN] x10^3	Conversion, %	Polymer Counted, mg	SAP x10^{-6}a	k_H/k_T
10-1	100	-	94.4	38.8	3.61	
-2				38.3	3.63	
-3				44.7	3.60	-
-4				47.7	3.57	
8-1	60	9.71	5.8	35.8	3.51	
-2				35.9	3.48	1.04_3
-3				35.2	3.46	
9-1	60	9.71	5.7	36.0	3.49	
-2				40.3	3.47	1.04_3
-3				53.2	3.47	
7-1	100	-	7.9	34.3	3.48	
-2				42.7	3.52	
-3				39.1	3.48	1.04_2
-4				35.1	3.46	
-5				31.7	3.48	
-6				47.5	3.47	

[a]In disintegrations per minute per gram(DPM/g).

Table III. Isotope Effects for Styrene-β-t at 60 and 100°

No.	Temperature, °C	[AIBN] x10³	Conversion, %	Polymer Counted, mg	SAP x10⁻⁶a	k_H/k_T
108-1	100	-	91.9	46.9	5.35	
-2				43.6	5.39	
-3				57.9	5.36	
-4				35.5	5.37	-
-5				47.6	5.33	
-6				33.8	5.41	
109-1	60	-	5.9	43.0	5.47	
-2				39.7	5.49	0.97_0
-3				38.2	5.52	
103-1	60	6.15	7.5	33.6	5.50	
-2				37.5	5.48	0.96_9
111-1	60	0.46	11.7	52.8	5.49	
-2				41.6	5.48	
-3				40.3	5.48	
-4				36.5	5.54	0.96_5
-5				35.5	5.57	
-6				40.0	5.54	
115-1	100	-	10.0	42.0	5.45	
-2				41.2	5.44	0.97_4
-3				47.8	5.49	

[a]In disintegrations per minute per gram(DPM/g).

Table IV. Isotope Effects for Styrene-p-t at 60 and 100°

No.	Temperature, °C	[AIBN] x10^3	Conversion, %	Polymer Counted, mg	SAP x10^{-6}a	k_H/k_T
50-1	100	9.71	94.4	38.1	4.28	
-2				39.1	4.24	
-3				34.8	4.25	-
-4				40.1	4.23	
51-1	60	3.05	8.9	33.3	4.22	
-2				34.8	4.20	1.00_2
-3				29.8	4.25	
52-1	60	-	3.6	33.9	4.22	
-2				26.9	4.25	1.00_1
-3				28.2	4.24	
53-1	100	-	8.7	34.2	4.22	
-2				29.9	4.26	1.00_0
-3				29.4	4.25	
54-1	100	-	8.0	33.9	4.27	
-2				36.9	4.25	1.00_0
-3				34.4	4.23	

[a]In disintegrations per minute per gram(DPM/g).

Table V. Summary of Isotope Effects in the Polymerization of Styrene-α-t, -β-t, and -p-t

Monomer	60°	100°
Styrene-α-t	1.04_3	1.04_2
Styrene-β-t	0.96_8	0.97_4
Styrene-p-t	1.00_1	1.00_0

Table VI. Isotope Effects for Styrene-β-t in the Presence of Various Diluents at 60°

No.	[Styrene]	Diluent	[AIBN] x10^3	Conversion, %	Polymer Counted, mg	SAP$_{-6a}$ x10^{-6}a	k_H/k_T
112-1	2.15	Benzene	4.60	10.4	37.3	5.50	
-2					42.9	5.47	0.96_6
-3					35.7	5.53	
110-1	4.30	Methanol	4.60	6.2	43.1	5.52	
-2					42.4	5.50	0.96_5
-3					40.6	5.51	
102-1	2.15	Methanol	4.60	5.4	28.1	5.44	
-2					26.3	5.47	0.97_1
114-1	1.72	Methanol	3.70	14.8	62.4	5.48	
-2					41.7	5.53	
-3					42.7	5.54	
-4					33.6	5.53	0.96_5
-5					41.9	5.48	
-6					38.9	5.50	
116-1	2.15	Nujol	4.60	21.1	34.9	5.50	
-2					54.9	5.44	0.97_0
-3					35.5	5.48	

[a] In disintegrations per minute per gram(DPM/g).

The isotope effect k_H/k_D in reaction 3, in which an unlabeled

$$M_n\cdot + \text{Styrene} \xrightarrow{k_H} M_{n+1}\cdot \qquad (3a)$$

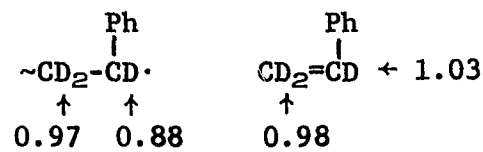
$$M_n\cdot + \text{Styrene-}\underline{d} \xrightarrow{k_D} M_{n+1}\cdot \qquad (3b)$$

polystyryl radical attacks normal or deuteriostyrene, can be calculated from the k_H/k_T ratio through use of the Swain equation (eq 4).[4] Attack by an unlabeled polymer radical on styrene-$\underline{\beta}$-$\underline{d}$ has

$$k_H/k_D = (k_H/k_T)^{1/1.442} \qquad (4)$$

a calculated k_H/k_D of 0.98. For two $\underline{\beta}$-deuteriums this value is squared: $(0.98)^2 = 0.96$. Since the overall effect in the polymerization of styrene-$\underline{\beta}$-$\underline{d}$ is 0.89,[3] then each deuterium substituted $\underline{\beta}$ to the radical leads to an inverse effect of 2%. The effect of $\underline{\alpha}$-deuterium substitution in the radical can be calculated similarly from the isotope effects observed in the polymerization of styrene-$\underline{\alpha}$-$\underline{t}$ and -$\underline{\alpha}$-$\underline{d}$. The contribution of each deuterium to the isotope effect on the propagation step in the polymerization of styrene is shown below:

Isotope Effects, k_H/k_D (per deuterium)



These data should replace those on p 1204 in reference 3.

We observed a normal isotope effect (i.e., $k_H/k_D > 1$) for a deuterium substituted at a carbon which goes from an olefinic to a radical center, indicating that in the polymerization of styrene, the C_α-H bond is weakened in the transition state.[5] A nominal sp^2 hybridization is maintained throughout reaction, and it has generally been assumed that there is no effect at such a position. The observation of a normal isotope effect at C_α appears to have a direct bearing on the interpretation of the isotope effects observed in cycloadditions. A brief background of this area follows.

APPLICATION OF THE PRESENT RESULTS TO CYCLOADDITIONS

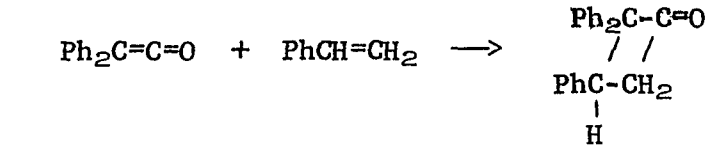
Secondary kinetic isotope effects have been observed in radical additions to deuterated olefins (see Part I, Chapter 1).[3,6,7] Substitution of a deuterium at a carbon undergoing an sp^2 to sp^3 hybridization change during reaction (C_β in eq 5) leads to an inverse effect of about 3-5% (k_H/k_D = 0.95-0.97). The effect at a carbon

$$R\cdot + C_\beta{=}C_\alpha\text{-}X \longrightarrow R\text{-}C_\beta\text{-}\dot{C}_\alpha\text{-}X \qquad (5)$$

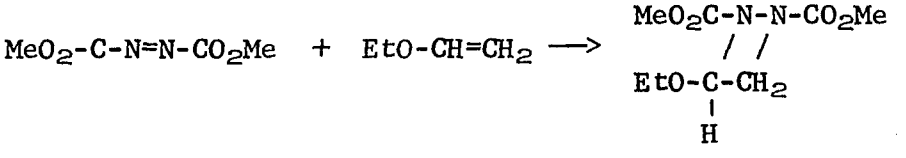
going from an olefinic to a radical center (C_α in eq 5) previously was assumed to be negligible, whereas we find a normal effect ($k_H/k_D > 1$) for such a transition in the polymerization of styrene. These effects should be useful as sensitive probes in mechanistic studies of cycloadditions in determining the exact timing of bond-formation; that is, whether reaction proceeds by a concerted process, or by a two-step, radical mechanism.[8a] A concerted process

should lead to an inverse effect at each end of the double bond. The secondary isotope effects expected for a two-step mechanism are taken from those observed in radical additions to olefins, namely, an inverse effect at C_β and a normal effect at C_α.

Table VII shows that the isotope effects at the β carbon in the reaction of styrene with diphenylketene (eq 6)[9a] and of ethyl vinyl



(6)



(7)

ether with methyl azodicarboxylate (eq 7)[9b] are inverse, as anticipated. In both reactions, however, the effect at C_α is normal. Gustorf, et al.[9b] conclude that the azodicarboxylate-vinyl ether reaction is two-step, and do not comment on the normal effect. On the other hand, Baldwin and Kapecki[9a] attribute the normal effects in both systems to a weakening of the C_α-H bond in the transition state by orbital interaction between that bond and the p orbital in the unlabeled olefin; these authors conclude that both reactions proceed by a concerted process, stating that "something quite noticeable through isotope effects is happening at both carbons in the transition states of these reactions." Stereospecificity and lack of an appreciable solvent effect on rate are observed in the

Table VII. Secondary Isotope Effects in Cycloadditions

Reaction			k_H/k_D [a]	Reference
$Ph_2C{=}C{=}O$	+	PhCH=CHD	0.91	b
$Ph_2C{=}C{=}O$	+	$PhCD{=}CH_2$	1.23	b
$CH_3O_2C{-}N{=}N{-}CO_2CH_3$	+	EtO-CH=CHD	0.83	c
$CH_3O_2C{-}N{=}N{-}CO_2CH_3$	+	$EtO{-}CD{=}CH_2$	1.11	c

[a] k_H refers to the [2 + 2] cycloaddition of unlabeled reactants; k_D refers to the reaction shown. [b] J. E. Baldwin and J. A. Kapecki, J. Amer. Chem. Soc., 92, 4874 (1970). [c] E. K. von Gustorf, D. White, J. Leitich and D. Henneberg, Tetrahedron Lett., 3113 (1969).

two cycloadditions;[9] these results, though compatible with a one-step mechanism, are only indicative evidence rather than conclusive proof of concertedness.[10a,10b]

It is notable that each case in which a normal isotope effect is observed, the carbon involved is at a position which would go from an olefinic to a radical center if the process were a two-step, radical reaction (C_α in eqs 6 and 7). Our results indicate that the hydrogen isotope effect at a carbon undergoing such a transition is in a normal direction. Thus the normal isotope effects in the diphenylketene-styrene and azo ester-vinyl ether cycloadditions may be rationalized in terms of a two-step, radical mechanism.[11] If a two-step process is operative, the rate of ring closure of the diradical must be much greater than the rate of rotation around the C_α-C_β bond, since stereospecificity is observed.[9]

The inverse effects at C_β and the normal effects at C_α in the cycloadditions discussed above are much larger than those in comparable radical reactions. There is evidence that this may be true generally; for example, Kirchner and Buchholz[12] studied the effect of α-deuterium substitution in the dimerization of styrene to give 1,2-diphenylcyclobutane. If a two-step, radical mechanism is postulated (eq 8),[13] in which k_2 is much larger than k_1, a normal isotope effect would be expected if deuterium were substituted at the

$$2\ PhCH{=}CH_2 \xrightarrow{k_1} \begin{array}{l} H \quad H \\ | \quad | \\ PhC\cdot \quad \cdot CPh \\ / \quad / \\ H_2C - CH_2 \end{array} \xrightarrow{k_2} \begin{array}{l} H\ H \\ |\ | \\ PhC\text{-}CPh \\ /\ / \\ H_2C\text{-}CH_2 \end{array} \qquad (8)$$

α position. The authors report that in the case of styrene-α-d, $k_H/k_D = 1.2$, i.e., an effect of about 10% per deuterium. It appears, then, that the isotope effects in cycloadditions generally are much larger than those associated with radical additions to labeled olefins.

Normal deuterium isotope effects of an appreciable magnitude have been observed in other systems,[14] but these effects are a measure of the isotope effect on a product-forming rather than a rate-determining step.

USE OF TRITIUM-LABELED STYRENES IN COPOLYMERIZATION STUDIES

The copolymerization equation is[15]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (9)$$

where $[M_1]$ and $[M_2]$ are the concentrations of the comonomers M_1 and M_2, $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$. The rate constants are defined in equations 10-13.

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\text{-}M_1\cdot \qquad (10)$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_1\text{-}M_2\cdot \qquad (11)$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_2\text{-}M_1\cdot \qquad (12)$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\text{-}M_2\cdot \qquad (13)$$

The comonomers maleic anhydride(M_1) and styrene(M_2) were first reported by Alfrey and Lavin[16] to form a perfectly alternating copolymer when $[M_1]/[M_2] \geq 20$. When maleic anhydride is present in large excess, essentially the only reactions occurring are those given in eqs 11 and 12, that is, attack on one monomer by a polymeric radical ending in the other monomer. Therefore in a copolymerization system involving a perfectly alternating copolymer, it is possible to determine the isotope effect on the cross-propagation step in which the growing polymeric chain ending in the unlabeled comonomer attacks the labeled monomer (eq 14). The equation for k/k^* is given in eq 15.[1,2]

$$\sim M_1\cdot + M_2 \xrightarrow{k} \sim M_1\text{-}M_2\cdot \qquad (14a)$$

$$\sim M_1\cdot + M_2^* \xrightarrow{k^*} \sim M_1\text{-}M_2^*\cdot \qquad (14b)$$

$$k/k^* = \frac{\ln(1 - f_i)}{\ln(1 - r_i f_i)} \qquad (15)$$

where r_i is the ratio of the specific activity of the copolymer $(SAP)_i$ at macroscopic fraction conversion f_i to that of the monomer (SAM). At 100% conversion (f = 1.00) SAP. is equal to SAM times the macroscopic weight fraction of the labeled monomer in the copolymer.[17]

The data from the radical-initiated copolymerization of maleic anhydride and styrene-$\underline{\beta}$-$\underline{t}$ are shown in Table VIII. There is no

Table VIII. Isotope Effect for Maleic Anhydride(MA) and Styrene-β-t Copolymerization at 60°

No.	mole fraction MA	AIBN, mg	Diluent, ml	Temperature, °C	Conversion, %[a]	Copolymer Counted, mg	SAP x10^{-6}[b]	k_H/k_T
121-1	0.958	1.51	7.0[c]	60	100.	34.3	2.33	
-2						20.5	2.27	
-3						30.7	2.31	-
-4						32.9	2.35	
-5						36.1	2.33	
123-1	0.977	6.06	200.[d]	80	100.	31.6	2.33	
-2						35.5	2.31	-
-3						39.3	2.37	
120-1	0.954	1.51	9.0[c]	60	16.2	36.7	2.29	
-2						36.6	2.36	
-3						42.3	2.35	1.00_0
-4						35.5	2.32	
122-1	0.978	9.09	250.[d]	60	12.0	33.9	2.33	
-2						42.2	2.35	1.00_0
-3						32.1	2.31	

[a]Based on styrene conversion. [b]In disintegrations per minute per gram(DPM/g). [c]Acetone as diluent. [d]Benzene as diluent.

kinetic isotope effect in the copolymerization, i.e., $k_H/k_T = 1.00$ vs. $k_H/k_T = 0.97$ in the homopolymerization of styrene-β-t. This result is in accord with the Hammond postulate,[18] which states that in a series of related exothermic reactions, those with lower activation energies involve less bond reorganization in the transition state. In this case, a smaller isotope effect is associated with a lower activation energy. Resonance forms like Ib lower the activation energy for addition to styrene monomer by a polymeric

$$[\sim MA\cdot \quad \dot{C}H_2\text{-}\dot{C}HPh \quad \longleftrightarrow \quad \sim MA\text{:}^- \quad \dot{C}H_2\text{-}\overset{+}{C}HPh]$$

Ia Ib

radical having an anhydride end unit compared to that for polystyryl radical addition to styrene, and therefore the isotope effect on the cross-propagation step is expected to be more nearly unity. Similarly, Hodnett and Jensen[19] have reported that the isotope effect k_{12}/k_{14} decreases from 1.09 to 1.05 in going from homopolymerization of styrene-β-^{14}C to copolymerization with maleic anhydride.

Recently Gaylord[20] presented evidence which indicates that the mechanism of copolymerization in strongly alternating systems actually consists of the polymerization of a charge transfer complex, rather than repeated cross-propagation steps in which free monomers are added to the growing copolymeric chain. Gaylord proposed that the comonomers, one with electron donor tendencies and the other with electron acceptor tendencies, come together to form a dipolar,

diradical charge transfer complex (CTC) as shown in eq 16a, after which the complex itself undergoes polymerization (eq 16b).

$$CH_2{=}CHPh + CH_2{=}CHX \rightleftharpoons \left[\begin{array}{l} CH_2\text{-}\overset{\cdot}{C}\overset{+}{H}PH \\ \\ \overset{\cdot}{C}H_2\text{-}\overset{-}{C}HX \end{array} \right] \qquad (16a)$$

(CTC)

$$M_n\cdot + CTC \longrightarrow M_{n+1}\cdot \qquad (16b)$$

At low monomer concentrations, equilibrium would be shifted away from the complex; however, even in dilute solution polymerization of the CTC might be important. We studied the copolymerization of maleic anhydride and styrene-t at both high and low monomer concentrations and found that $k_H/k_T = 1.00$ in both cases. If complex formation is an important reaction in the copolymerization of styrene and maleic anhydride, it would appear from our results that for styrene-β-t the isotope effect on the equilibrium in eq 16a is negligible.

Secondary kinetic hydrogen isotope effects are generally small, and therefore monomers labeled with hydrogen isotopes should be very useful in determining reactivity ratios in the copolymerization of a labeled monomer with various comonomers.[22,23] We utilized styrene-β-t and -p-t in a copolymerization of each with maleic anhydride in

order to determine the reactivity ratios for the system maleic anhydride(M_1)-styrene(M_2).

The copolymerization equation was previously given in equation 9.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (9)$$

At low conversions, $[M_1]$ and $[M_2]$ do not change appreciably during reaction, and $d[M_1]/d[M_2]$ can be approximated by

$$\frac{d[M_1]}{d[M_2]} = C \qquad (17)$$

where C is the ratio of $[M_1]$ to $[M_2]$ in the initially formed copolymer. The ratio $[M_1]/[M_2]$ in the feed is defined to be F, and eq 9 becomes

$$C = F \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \qquad (18)$$

Rearrangement of eq 18 leads to eq 19.

$$r_2 = \frac{F^2}{C} r_1 + F(C^{-1} - 1) \qquad (19)$$

Each copolymerization run provides a value of both F and C for use in equation 19. Since two unknowns, r_1 and r_2, remain, no unique value for either r_1 or r_2 can be calculated. That is, each

run gives only a line on an r_1-r_2 plot. Several runs with different values of F are necessary to obtain r_1 and r_2, as determined by the line intersection pattern. Table IX gives the data for maleic anhydride copolymerization with styrene-β-t and -p-t, and Figure 1 shows the corresponding r_1-r_2 graph. The results indicate that r_1 and r_2 are 0.008 ± 0.005 and 0.088 ± 0.005, respectively. Values of r_1 and r_2 observed by other workers are listed in Table X.

It is necessary that k_{11}, i.e., k_p for maleic anhydride polymerization, be non-zero if r_1 is to be finite. Usually 1,2-disubstituted monomers undergo polymerization only very reluctantly,[24] presumably due to kinetic rather than thermodynamic considerations. Apparently steric interaction between the substituents on the radical and monomer inhibits polymerization to such an extent that competing reactions (e.g., chain transfer, termination) become important. However, in the case of maleic anhydride, Lang, et al.[25] and later Joshi[26] have reported the isolation of polymeric material resulting from self-addition.[27] Joshi[26] used benzoyl peroxide to initiate polymerization and found polymer with molecular weights as high as 1150. Also he showed that δ ($= k_t^{1/2}/k_p$) is finite and has a value of about 109.

Our value of r_2 is much larger than that generally reported (see Table X). The reason for this difference is not clear. We monitored styrene content by a radiotracer method, whereas the other workers determined copolymer composition by titration of the anhydride units. Incomplete titration of the anhydride units would lead to a higher value of r_2, but except for Huglin,[28] workers using

Table IX. Values of F (= $[M_1]/[M_2]$ in the feed) and C (= $[M_1]/[M_2]$ in the copolymer) for the Copolymerization of Maleic Anhydride(M_1) and Tritiated Styrene(M_2) at 60°

No.	F_{avg}[a]	AIBN, mg	Diluent, ml	Conversion, %[b]	Copolymer Counted, mg	SAP $\times 10^{-6}$[c]	C
122-1[d]	43.3	9.09	250.[e]	12.0	33.9	2.33	1.04
-2					42.2	2.35	
-3					32.1	2.31	
120-1[d]	22.3	1.51	9.0[e]	16.2	36.7	2.29	
-2					36.6	2.36	1.04
-3					42.3	2.35	
-4					55.5	2.32	
124-1[d]	1.08	3.03	200.[e]	4.2	29.0	2.83	
-2					20.2	2.83	0.94
-3					21.5	2.79	
160-1[f]	0.492	1.51	200.[g]	2.6	26.9	2.08	
-2					22.0	2.12	0.83
-3					27.7	2.08	

[a]This column shows the ratio of the average concentrations of M_1 and M_2 during reaction. [b]Based on styrene conversion. [c]In disintegrations per minute per gram(DPM/g). [d]Styrene-β-t. [e]Acetone as diluent. [f]Styrene-p-t. [g]Benzene as diluent.

Figure 1. Plot of r_1 *versus* r_2 for the System Maleic Anhydride(M_1)-Styrene(M_2)

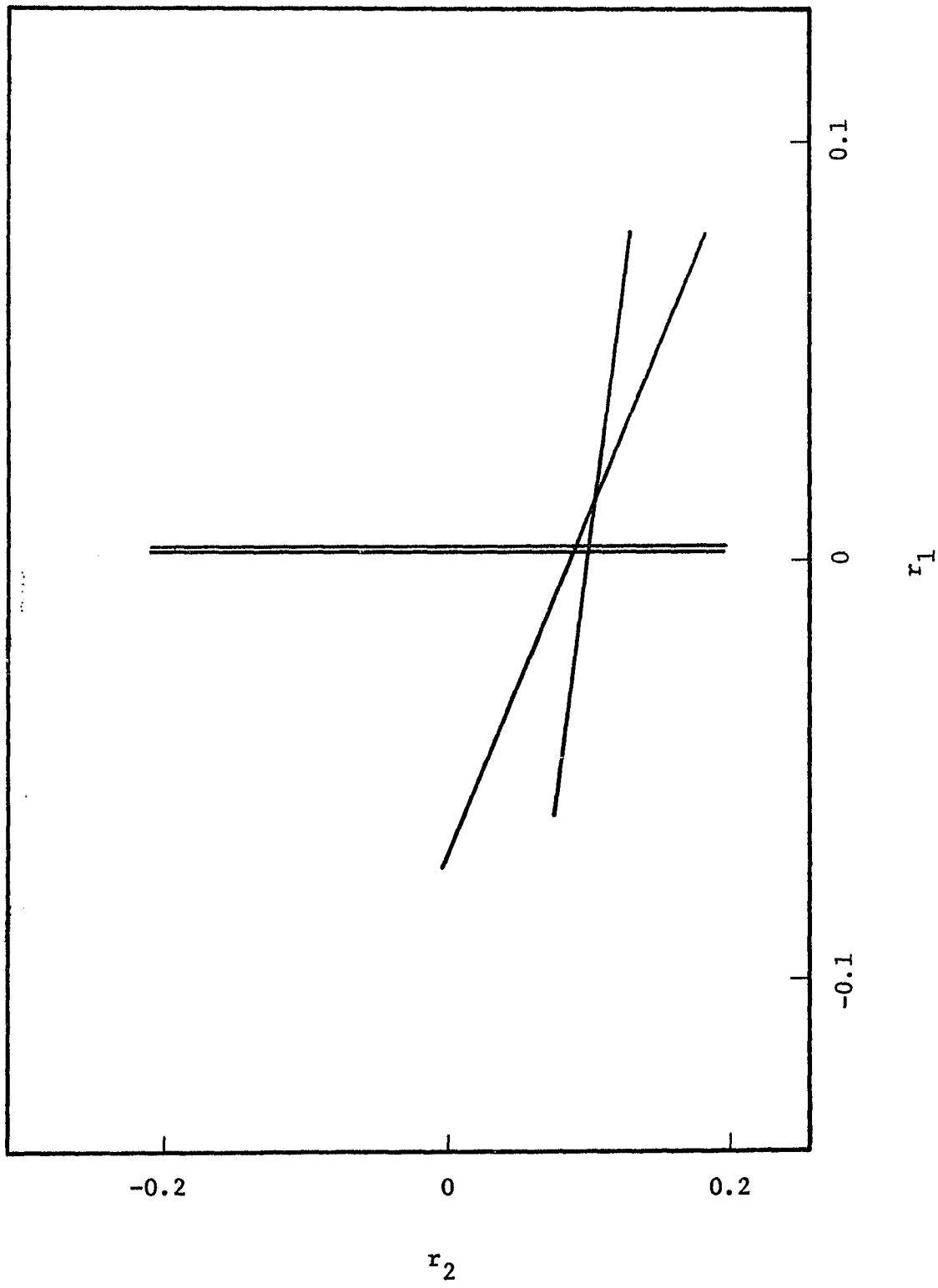


Table X. Compilation of r_1 and r_2 Values Observed in the Radical Copolymerization of Maleic Anhydride(M_1) and Styrene(M_2)

r_1	r_2	Temperature, °C	Solvent	Polymer Precipitates	Reference
0	0.042 ± 0.008	80	a	yes	k
0	0.01	60	b	not reported	l
0	0.01	60	c	no	m
0	0.01	60	d	e	n
0	0.022	60	b,f	e	n
0	0.029	60	g	e	n
0	0.019	50	h	no	o
0.015	0.040	50	i	no	p
0 ± 0.002	0.097 ± 0.002	50	i	no	q
0.008 ± 0.005	0.088 ± 0.005	60	a,i	j	this work

[a]Benzene. [b]None. [c]Styrene:methyl propyl ketone used in the ratios 12:88, 25:75 and 50:50. [d]50-50 styrene-decane. [e]Dependent upon the relative monomer concentrations; the reactivity ratios are unchanged regardless. [f]50-50 o-dichlorobenzene-styrene. [g]75-25 o-dichlorobenzene-styrene. [h]p-Dioxane. [i]Acetone. [j]Includes both homogeneous and heterogeneous polymerization conditions. [k]T. Alfrey and E. Lavin, J. Amer. Chem. Soc., 67, 2044 (1945). [l]C. Walling, E. Briggs and K. Wolfstirn, ibid., 70, 1543 (1948), footnote 11. [m]W. Barb, J. Polym. Sci., 11, 117 (1953). [n]C. H. Bamford and W. Barb, Disc. Faraday Soc., 14, 208 (1953). [o]T. Ang and H. Harwood, Polym. Preprints, 5, 306 (1964). [p]K. Noma, M. Niwa and K. Iwasaki, Kobunshi Kagaku, 20, 646 (1963), through Chem. Abstr., 60, 14518c. [q]M. B. Huglin, Polym., 3, 335 (1962).

this technique obtain lower values of r_2 than we do. Differences in solvent polarity should not affect r_1 and r_2 appreciably, though temperature may have a slight affect. The copolymer precipitated during reaction in some of the studies. Our runs, though, included both types of media, _viz._, benzene, a precipitating solvent, and acetone, one in which the copolymer is soluble.

As Huglin[28] has pointed out, a value of r_2 greater than 0.04 tends to bring the point for methyl radical addition to maleic anhydride into line on Szwarc's methyl affinity plot[29] of $\log(1/r_2)$ against $\log(k_2/k_1)$. Here, k_1 and k_2 are the rate constants for reactions 20 and 21.[30]

$$\text{Me}\cdot + \text{RH} \xrightarrow{k_1} \text{MeH} + \text{R}\cdot \qquad (20)$$

$$\text{Me}\cdot + \text{M} \xrightarrow{k_2} \text{Me-M}\cdot \qquad (21)$$

In studies of copolymer compositions, Barb[31] and Ham[32] examined copolymerization penultimate effects, in which the selectivity of the copolymeric radical is affected by non-terminal units. They used an equation derived by Merz, Alfrey and Goldfinger[33] which includes rate constants that allow for the effect of penultimate units, _e.g._, equations 22 and 23. Barb[31] and Ham[32] applied this

$$\sim M_1\text{-}M_2\cdot + M_1 \xrightarrow{k_{121}} \sim M_1\text{-}M_2\text{-}M_1\cdot \qquad (22)$$

$$\sim M_1\text{-}M_2\cdot + M_2 \xrightarrow{k_{122}} \sim M_1\text{-}M_2\text{-}M_2\cdot \qquad (23)$$

analysis to the maleic anhydride-styrene system and obtained various rate constants of the k_{121} and k_{122} type. However, Joshi[34] has reported that inclusion of a finite, though small, value of r_1 gives a calculated composition curve that is in close agreement with the experimental data. Also, Berger and Kuntz[35] have shown that sequence distribution, not copolymer composition, provides a basis for selecting the correct copolymerization model, that is, penultimate or terminal. Ang and Harwood[36] determined the sequence distribution in a series of styrene-maleic anhydride copolymers, and concluded that the terminal model adequately explained their results, whereas the penultimate model led to incorrect predictions. It appears, therefore, that there are only two reactivity ratios, r_1 and r_2, that need be investigated in the system maleic anhydride(M_1)-styrene(M_2), and that r_1 is not identically zero, as generally has been assumed.

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one mechanism may be acting simultaneously in cycloadditions. For example, Huisgen and Otto[8b] have suggested that the reaction of dimethylketene with N-isobutenylpyrrolidine to give a cyclobutanone proceeds by synchronous and stepwise paths; (b) R. Huisgen and P. Otto, J. Amer. Chem. Soc., 91, 5922 (1969).

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CHAPTER 4

APPENDIX A

The equation for k_H/k_T is[1,2]

$$k_H/k_T = I = \frac{\ln(1 - f_i)}{\ln(1 - r_i f_i)} \qquad (1)$$

where r_i is the ratio of the specific activity of the polymer(SAP_i) at (low) fraction conversion f_i to that of the monomer(SAM). The specific activity of high-conversion polymer(SAP_{hc}) is very nearly that of SAM, and thus the first approximation to I is given in eq 2.

$$I \cong I_{approx} = \frac{\ln(1 - f_i)}{\ln(1 - \frac{SAP_i}{SAP_{hc}} f_i)} \qquad (2)$$

Then I_{approx} is used in eq 3[1,2] to get a value for $r_{hc,approx}$, which

$$r_{hc} = \frac{SAP_{hc}}{SAM} \cong r_{hc,approx} = \frac{1}{f_{hc}} [1 - (1 - f_{hc})^{1/I_{approx}}] \qquad (3)$$

is subsequently used to get a better approximation to SAM through the relationship given in eq 4.

$$SAM \cong SAM_{approx} = \frac{SAP_{hc}}{r_{hc,approx}} \qquad (4)$$

Use of SAM_{approx} in eq 1 yields a second approximation to I, I'_{approx}, and the calculations are repeated. Several iterations are necessary to achieve self-consistency.

Sample Calculation

Substituting SAP_i/SAM for r_i in eq 1 gives eq 5. The only

$$k_H/k_T = I = \frac{\ln(1 - f_i)}{\ln(1 - \frac{SAP_i}{SAM} f_i)} \qquad (5)$$

unknown on the right-hand side of eq 5 is SAM; SAP_i is the specific activity of a low-conversion polymer and f_i is the macroscopic fraction conversion of that polymer. SAP_{hc} is substituted for SAM, and eq 2 is used to begin the series of calculations.

The data from runs 8 and 10, low and high conversions, respectively, in Table III of Chapter 3 will be used to calculate I.

$f_i = 0.0581$ $\quad SAP_i = 3.48 \times 10^6$ DPM/g

$f_{hc} = 0.944$ $\quad SAP_{hc} = 3.60 \times 10^6$ DPM/g

$$I_{approx} = \frac{\ln(1 - 0.0581)}{\ln(1 - \frac{3.48 \times 10^6}{3.60 \times 10^6} \cdot 0.0581)} \quad (6a)$$

$$= 1.035 \quad (6b)$$

It is necessary to correct SAP_{hc} (using r_{hc}) since it is smaller than SAM.

$$r_{hc,approx} = \frac{1}{f_{hc}} [1 - (1 - f_{hc})^{1/I_{approx}}] \quad (3)$$

$$= \frac{1}{0.944} [1 - (0.056)^{1.035}] \quad (7a)$$

$$= 0.994 \quad (7b)$$

So we find

$$SAM_{approx} = \frac{SAP_{hc}}{r_{hc,approx}} = \frac{3.60 \times 10^6 \text{ DPM/g}}{0.994} \quad (8a)$$

$$= 3.63 \times 10^6 \text{ DPM/g} \quad (8b)$$

The second (and closer) approximation to I, I'_{approx}, is given by

$$I'_{approx} = \frac{\ln(1 - f_i)}{\ln(1 - \frac{SAP_i}{SAM_{approx}} \cdot f_i)} \quad (9a)$$

$$= 1.040 \quad (9b)$$

and that for r_{hc}, $r'_{hc,approx}$, is given by

$$r'_{hc,approx} = \frac{1}{f_{hc}} [1 - (1 - f_{hc})^{1/I'_{approx}}] \quad (10a)$$

$$= 0.993 \quad (10b)$$

The next approximation for SAM is given in eq 11.

$$SAM'_{approx} = \frac{SAP_{hc}}{r'_{hc,approx}} = \frac{3.60 \times 10^6 \text{ DPM/g}}{0.993} \quad (11a)$$

$$= 3.64 \times 10^6 \text{ DPM/g} \quad (11b)$$

The final result is:

$$k_H/k_T = I = 1.04_3 \quad (12)$$

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CHAPTER 5
APPENDIX B

If styrene-t and inactive maleic anhydride are copolymerized, the specific activity of the copolymer(SAC) is given by eq 1.

$$SAC = SAM \frac{(1 - f)}{(1 - f)\ MW_{RM} + (f)\ MW_{IM}} \quad (1)$$

where SAC is the specific activity of the copolymer in DPM/g, SAM is the specific activity of the radioactive monomer(RM) in DPM/mole, f is the mole fraction of the inactive monomer(IM) in the copolymer, MW_{RM} is the molecular weight of the labeled monomer, and MW_{IM} is the molecular weight of the inactive monomer. Equation 1 can be rearranged to eq 2, a form more suitable for calculation of f.

$$f = \frac{SAM - SAC\ (MW_{RM})}{SAM + SAC\ (MW_{IM} - MW_{RM})} \quad (2)$$

The data from run 120 in Table IX of Chapter 3 will be used to calculate f, which in turn will be used to calculate C (= [maleic anhydride]/[styrene] in the copolymer).

SAC	$= 2.33 \times 10^6$ DPM/g	MW_{RM}	= 104.1 g/mole
SAM	$= 5.55 \times 10^8$ DPM/mole	MW_{IM}	= 98.1 g/mole

F = 22.3 = [maleic anhydride]/[styrene] in the feed

The equation for f is

$$f = \frac{(5.55 - 2.33 \times 1.04) \times 10^8}{(5.55 - 2.33 \times 0.26) \times 10^8} \quad (3a)$$

$$= 0.509 \quad (3b)$$

Therefore C = 0.509/0.491 = 1.037. The values for C and F are substituted in eq 4, which gives the equation for one line on an r_1-r_2 plot.

$$r_2 = \frac{F^2}{C} \cdot r_1 + F(C^{-1} - 1) \quad (4a)$$

$$= 480\ r_1 - 0.78 \quad (4b)$$

PART II. HYDROGEN ATOM REACTIONS IN SOLUTION

CHAPTER 1
INTRODUCTION

GENERAL DISCUSSION

Reactions of the hydrogen atom in the gas phase have been extensively studied,[1,2] but the solution chemistry of this radical has come under intensive investigation only recently.[3-6] The hydrogen atom is of great theoretical interest; for example, data on its reactions are necessary to test calculations of absolute rate theory.[2] Also, it is desirable to compare the features of the H-atom with those of other free radicals. On a more pragmatic level, radiolysis studies have implicated this radical in radiation chemistry and biology.[4-6] In the radiolysis of aqueous solutions, the H-atom is produced along with various other species; e.g., the solvated electron and other ion radicals, other free radicals such as the hydroxyl radical, and excited molecules.[7] In order to interpret the chemical effects resulting from radiation, it is essential that the reactions of the different transient species be isolated and studied independently.

AQUEOUS RADIOLYSIS STUDIES

A number of different techniques have been used to study the reactions of hydrogens generated by the radiolysis of aqueous solutions. Scholes and Simic[5d] utilized a competitive system in which the hydrogen atoms reacted with $DCOO^-$ or different solutes(QH) to give HD (eq 1) and H_2 (eq 2). They measured the HD and H_2 yields for various

$$H\cdot + DCOO^- \longrightarrow HD + \cdot COO^- \quad (1)$$

$$H\cdot + QH \xrightarrow{k_2} H_2 + Q\cdot \quad (2)$$

concentrations of QH, and were able to obtain relative rate of reaction 2 for various substrates. The authors report that added N_2O, an electron scavenger, reduces the yields of HD and H_2, but k_2 remains constant whether or not N_2O is present. Two other systems, both similar to that of Scholes and Simic, have been developed. In one,[5f] $Fe(CN)_6^{-3}$ is used as the standard reactant (eq 3), and in the other,[5e] 2-propanol-2-$\underline{d}_1$ is used as the standard (eq 4). As Table I

$$H\cdot + Fe(CN)_6^{-3} \longrightarrow H^+ + Fe(CN)_6^{-4} \quad (3)$$

$$H\cdot + (CH_3)_2CDOH \longrightarrow HD + (CH_3)_2\dot{C}OH \quad (4)$$

shows, the results from the three methods are in good agreement.

ORGANIC SOLUTION RADIOLYSIS STUDIES

In the initial organic solution studies, hydrogen atoms were generated through use of high energy radiation. For example, Hardwick[4] utilized the radiolysis of hexane(RH) solutions of various substrates(QH) to determine relative rates of addition and hydrogen abstraction by the hydrogen atom (eqs 5-9).

$$RH \xrightarrow{\text{radiolysis}} H_2 + \text{products} \quad (5)$$

$$RH \xrightarrow{\text{radiolysis}} H\cdot + \text{products} \quad (6)$$

$$H\cdot + RH \longrightarrow H_2 + R\cdot \quad (7)$$

Table I. Relative Rates of Hydrogen Abstraction from QH by Hydrogen Atoms Generated by Radiolysis of Aqueous Solutions

QH	Relative Rate		
	Ref. a	Ref. b	Ref. c
Methyl alcohol	(1)	(1)	(1)
Ethyl alcohol	8.9	10.	10.
Isopropyl alcohol	30.	33.	31.
$HCOO^-$	89.	160.	-
CH_3COO^-	0.2	-	0.2
Ethylene glycol	5.8	-	4.4

[a]G. Scholes and M. Simic, J. Phys. Chem., 68, 1738 (1964). [b]J. Rabani, ibid., 66, 361 (1962). M. Anbar, D. Meyerstein and P. Neta, J. Chem. Soc., 572 (1966).

$$H\cdot + QH \xrightarrow{k_8} QH_2\cdot \qquad (8)$$

$$H\cdot + QH \xrightarrow{k_9} H_2 + Q\cdot \qquad (9)$$

where R· and Q· are the radicals that result when hydrogen is abstracted from RH and QH, and $QH_2\cdot$ is the radical produced when a H-atom adds to QH. Hardwick[11] used steady-state treatment for hydrogen atoms to obtain the following kinetic expression:

$$\frac{1}{G(H_2)_0 - G(H_2)} = \left(\frac{1}{G_2(H)}\right)(k_7/k_8)\frac{[RH]}{[QH]} + \frac{1}{G_2(H)}[(k_9/k_8) + 1] \qquad (10)$$

where $G(H_2)_0$ is the yield of H_2 in neat RH (G values are yields in molecules per 100 eV), $G(H_2)$ is the yield of H_2 when a substrate QH is present, $G_2(H)$ is the yield of H· <u>via</u> reaction 1, and k_i is the rate constant for the reaction given in equation i. A plot of $1/[G(H_2)_0 - G(H_2)]$ against [RH]/[QH] should give a straight line with a slope $(k_7/k_8)(1/G_2(H))$ and an intercept $(1/G_2(H))[(k_9/k_8 + 1]$. Hardwick studied a number of substrates and in all cases, obtained a linear relationship. From the slope he calculated the relative rate of addition to QH (eq 8), and from the intercept, the relative rate of abstraction from QH (eq 9). Representative data reported by Hardwick are given in Table II.

There are several surprising features to these results. For example, in the ketone series, the reactivity (per hydrogen) decreases in the order Ac-Me > Ac-Et > Ac-<u>i</u>-Pr, contrary to the order usually observed for other radicals ($3^o > 2^o > 1^o$).[8] A similar anomaly exists for ethylbenzene and cumene, in which case Hardwick's

Table II. Relative Rates of Hydrogen Abstraction from QH by Hydrogen Atoms Generated by Radiolysis of Organic Solutions

QH	Relative Rate[a]
Acetone	(1)
Methyl ethyl ketone	0.9
Methyl isopropyl ketone	0.4
Toluene	b
Ethylbenzene	0.7
Cumene	0.1
p-Xylene	b
tert-Butyl mercaptan	b
Diphenylmethane	b

[a]Data of T. J. Hardwick, J. Phys. Chem., 66, 117 (1962).

[b]This compound is relatively inert toward hydrogen abstraction.

values lead to a calculated $3^{o}:2^{o}$ reactivity ratio of 1:3. Also, he reported that compounds such as p-xylene and diphenylmethane are unreactive toward the hydrogen atom. Perhaps most damaging of all was the finding by Hardwick that tert-butyl mercaptan, a very good hydrogen donor, was inert to hydrogen abstraction.

Much work has been done in radiolysis subsequent to Hardwick's investigations, and it appears now that complications in Hardwick's system render his data invalid. Earlier, Schuler[9] had shown that low concentrations of solutes with high electron affinities could change the radiation chemical process. In a study of the radiolysis of aqueous solutions, Scholes and Simic[5d] used N_2O to scavenge electrons and found that the yield of molecular hydrogen was reduced correspondingly; similarly, they found that N_2O reduced the yield of hydrogen in the radiolysis of cyclohexane.[10] Apparently, then, the solvated electron is a viable species in both aqueous and organic solution radiolyses, and the electrons in these media are precursors to hydrogen atoms.

Holroyd[5a] has shown that some solutes that are very reactive toward the hydrogen atom are also excellent electron scavengers. Thus it appears that Hardwick was not isolating the reactions of the hydrogen atom, but rather his system contained a built-in source of error which varied with each solute he studied.

THIOL PHOTOLYSIS STUDIES

Pryor and coworkers[3] have studied the reactions of the hydrogen atom, using photolysis of thiols in organic solution as a convenient method of generating H-atoms in the absence of other reactive species

such as are produced in radiolysis. The first successful system developed in Pryor's laboratories (Method A) involves the photolysis of deuterated thiols to produce deuterium atoms.[3a] The deuterium atoms, presumably thermalized prior to reaction,[11] then abstract either deuterium or hydrogen from the thiol, or hydrogen from an organic hydrogen donor, QH. The reaction scheme is as follows:

Method A

$$RSD \xrightarrow{h\nu} RS\cdot + D\cdot \qquad (11)$$

$$D\cdot + RSD \xrightarrow{k_{12}} D_2 + RS\cdot \qquad (12)$$

$$D\cdot + RSD \xrightarrow{k_{13}} HD + \cdot RSD \qquad (13)$$

$$D\cdot + QH \xrightarrow{k_{14}} HD + Q\cdot \qquad (14)$$

$$Q\cdot + RSD \longrightarrow QD + RS\cdot \qquad (15)$$

$$2\ RS\cdot \longrightarrow RSSR \qquad (16)$$

where ·RSD is a thiol that has lost a hydrogen atom from its R group, and the other symbols have their usual meaning. At low conversions, reactions 15 and 16 can be neglected. Kinetic analysis of this system indicates that a plot of $[HD]/[D_2]$ *versus* $[QH]/[RSD]$ should yield a straight line of slope $k_H I_{14}$ (see eq 17), where $I_{14} = k_D/k_H$

$$\frac{[HD]}{[D_2]} = \frac{k_{13}}{k_{12}} + \frac{k_H I_{14}}{k_{12}} \frac{[QH]}{[RSD]} \qquad (17)$$

for hydrogen or deuterium atoms reacting with QH. Values of I_{14} are very nearly unity, and are essentially the same for all QH compounds. [9]

Using either thiophenol-$\underline{d}_1$ or 2-methyl-2-propanethiol-$\underline{d}_1$ as a source of deuterium atoms, Pryor and Stanley[3a] measured the relative reactivities of a number of organic hydrogen donors, and found agreement within about 10% for the two different thiols. Since the bond strengths of the S-H bonds in the two thiols differ by about 13 kcal/mol,[12] this agreement indicates that no reaction that involves making or breaking a bond to sulfur is interfering with the analysis.

A second, similar system (Method B) used by Pryor[3f] to measure the relative reactivities of organic compounds with hydrogen atoms involves the photolysis of tritiated thiol in the presence of a QH, and measuring the amount of tritium incorporated into the QH (eqs 18-23). The relative specific activities of recovered QH(t) and

Method B

$$RSH(t) \xrightarrow{h\nu} RS\cdot + H\cdot(t\cdot) \qquad (18)$$

$$H\cdot + QH \longrightarrow H_2 + Q\cdot \qquad (19)$$

$$H\cdot + Q'H \longrightarrow H_2 + Q'\cdot \qquad (20)$$

$$Q\cdot + RSH(t) \longrightarrow QH(t) + RS\cdot \qquad (21)$$

$$Q'\cdot + RSH(t) \longrightarrow Q'H(t) + RS\cdot \qquad (22)$$

$$Q\cdot + Q'H \longrightarrow QH + Q'\cdot \qquad (23)$$

Q'H(t) are directly related to their reactivities. One hydrogen donor is selected as the standard, and the reactivities of other compounds are determined by comparison of their specific activities with that of the standard.

There is an isotope effect on the steps in which activity is incorporated into the hydrogen donor (eqs 21 and 22). The magnitude of this isotope effect depends on the nature of the radical, [3] but should be relatively constant in a series of similar QH compounds. The reaction given in equation 23 potentially could lead to erroneous results, but is unimportant when excess thiol is present.

RESULTS FROM RADIOLYSIS AND THIOL PHOTOLYSIS SYSTEMS

Table III lists the results obtained by the two thiol methods for the reactivities of various organic compounds (relative to hexane) and also some of the data collected by radiolysis techniques. The data are in general agreement with the exception of the reactivities of the alcohols and the more reactive hydrocarbons as measured by radiolysis. The disagreement between the thiol systems and radiolysis for ethanol and 2-propanol cannot be attributed to experimental error, since a number of different workers have studied the radiolysis of the alcohols and have obtained similar results.

THE PRESENT CONTRIBUTION

In order to gain insight into the discrepancy between the results of the radiolysis methods and those of the thiol systems, we developed an independent technique that allowed us to study the reactions of the hydrogen atom kinetically. The details of this method and the implications of the results obtained from it are the subject of the remainder of Part II.

Table III. Relative Rates of Reaction of Hydrogen Atoms with Hydrogen Donors

QH	Method A[a]	Method B[b]	Radiolysis Ref. c	Radiolysis Ref. d
Hexane	(1)	(1)	-	(1)
Nonane	2.2	1.4	-	1.7
Dodecane	2.3	2.0	-	-
2,3-Dimethylbutane	2.2	2.1	-	3.2
2,4-Dimethylpentane	1.5	0.84	-	3.6
2,5-Dimethylhexane	2.4	1.2	-	-
Cyclopentane	1.2	0.87	-	1.1
Cyclohexane	1.2	1.1	-	-
Methyl alcohol	0.42	0.43	(0.42)	-
Ethyl alcohol	1.2	0.86	4.2	-
Isopropyl alcohol	1.9	1.8	13.2	-
tert-Butyl alcohol	0.03	<0.1	0.03	-
p-Dioxane	3.0	1.2	1.4	-
Tetrahydrofuran	9.1	-	7.7	-
Isopropyl ether	4.8	2.1	-	-

[a]Relative values of $k_H I_{14}$ obtained from the deuterated thiol system; see text. [b]Relative values of $k_H I_{21}$ obtained from the tritiated thiol system; see text. [c]Average values of data reviewed in M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotopes, 18, 493 (1967). [d]Data of T. J Hardwick, J. Phys. Chem., 65, 101 (1961).

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CHAPTER 2

EXPERIMENTAL SECTION

PREPARATIONS AND PURIFICATIONS

All solvents were dried and then distilled twice through an 11 cm column filled with Heli-pak; only the center fraction in each distillation was retained. Additionally, saturated hydrocarbons were passed through a silver nitrate-alumina column[1] to remove any unsaturated material. The ultraviolet spectra of these purified alkanes were taken on a Cary Model 14 Spectrophotometer and confirmed the absence of unsaturates.

Cumene was washed several times with concentrated sulfuric acid and then washed with water. After treatment with calcium chloride and magnesium sulfate, it was distilled (bp 44° at 18 mm). In some runs, other aromatic hydrocarbons purified by this method were used.

Methyl alcohol-d_1 and ethyl alcohol-d_1 were obtained from Diaprep, Incorporated (P.O. Box 1844, Atlanta, Ga.).

Isopropyl alcohol-d_1 and tert-butyl alcohol-d_1 were prepared by vigorously stirring the appropriate alcohol with 99.8% D_2O (purchased from ICN), then distilling the alcohol-d from the solution. The nmr spectra showed that five successive exchanges with equal volumes of D_2O were sufficient to bring the deuterium content at the exchangeable hydrogen position up to about 98-99% d. The alcohols were dried and distilled.

2-Methyl-2-propanethiol-d_1 was prepared in a similar fashion to the deuterated alcohols, except that since water and thiol are immiscible, it was not necessary to distill the thiol out in order

to effect a separation. After five exchanges the thiol was dried and distilled.

tert-Butyl peroxyformate (BUP).[2] A mixture of 50 ml of 90% tert-butyl hydroxide (Lucidol), 40 ml of 97% formic acid, 50 ml of pentane and 0.20 g of 4-tert-butylpyrocatechol was refluxed in the dark for 24 hr, while the water being formed was removed azeotropically through use of a Dean-Stark trap. Then 35 ml of water was added, and the mixture was extracted with 50 ml of pentane. The organic layer was separated and dried with magnesium sulfate. The solvent was removed under reduced pressure, and the residue distilled, giving 5.1 g of BUP [$H\text{-}CO_2\text{-}OC(CH_3)_3$], bp 43-44° at 25 mm. The infrared and nmr spectra showed that the BUP was free of alcohol, acid, hydroperoxide and peroxide. Because of the instability of BUP it was not possible to analyze for purity by gpc. Although BUP decomposes slowly at room temperature to tert-butyl alcohol and carbon dioxide (and some formic acid), decomposition can be inhibited by placing the perester at -78° under a nitrogen atmosphere. Under these conditions BUP can be stored for extended periods.

Deuterium gas (D_2) as purchased from the Matheson Co. contained only traces of deuterium hydride and hydrogen gas.

Deuterium hydride (HD) was generated by adding a solution of 99.8% d D_2O in butyl ether to a slurry of butyl ether and lithium aluminum hydride.[3] Analysis of the resulting gas by mass spectrometry indicated a composition of ~98% HD, and about 1% each of H_2 and D_2.

Silver nitrate-alumina. A slurry of 110 g of chromatographic

alumina (Alcoa Chemicals, F-20) and 200 ml of 1.5 M nitric acid was stirred vigorously for 30 min. The slurry was filtered through a coarse sintered-glass funnel, and the residue was washed with distilled water until all the acid was removed. A solution of 15 g of silver nitrate, 7 ml of water and 120 ml of methyl alcohol was used to wash the residue into a 500 ml round bottom flask, and the liquid phase was removed under reduced pressure. The residue was transferred to a 250 ml Erlenmeyer flask and dried at 140° for 24 hr. The finely divided, grayish material was poured into a column (13 mm x 20 cm) plugged at the bottom with glass wool.

KINETIC PROCEDURE

The ampoules used in these experiments were sealed to a male ℑ 12/30 ground glass joint. After the appropriate solution was added, the standard taper joint on the ampoule was connected to a unit consisting of a vacuum stopcock (Kontes Glass, 2 mm) sealed to a female ℑ 12/30 ground glass joint. This unit was then attached to a vacuum line, and the contents of the ampoule were degassed.

A solution of a hydrogen donor (QH) and thiol-d containing about 0.02 M BUP was placed in the specially adapted Pyrex ampoules and degassed by three freeze-pump-thaw cycles. Care was exercised to prevent cracking of the ampoules when a solvent with a very low melting point would freeze. To circumvent this difficulty the ampoule was turned to a near-horizontal position while the liquid nitrogen was being applied. The ampoule was then sealed off under vacuum by closing off the vacuum stopcock and irradiated for one hr

in a Rayonet photochemical reactor. Sixteen 3600 Å-region lamps (General Electric No. F8T5BL) provided illumination, and a merry-go-round apparatus was used to insure that all of the tubes received equal exposure to the light. After irradiation the samples were frozen in liquid nitrogen, degassed into a CEC Model 21-620 mass spectrometer, and analysis for H_2, HD and D_2 was made. Calibration curves were made for these gases using synthetic mixtures. Since machine reproducibility varied, it was necessary to run standards with the unknowns. In the case of the thiol-free system, treatment paralled that of the BUP-thiol-d system except that benzene replaced the thiol-d as diluent. Each hydrogen donor (benzene also) was irradiated under conditions similar to those used to photolyze the BUP solution; it was found that no hydrogen gas was produced in the photolysis of neat solvent.

PRODUCT ANALYSIS

As discussed above, H_2, HD and D_2 were determined by mass spectrometry, as were carbon dioxide and methane. Acetone and tert-butyl alcohol were determined by gpc (Aerograph 200, SE-30 column at 60°). In the analysis for formic acid, the sample was diluted with methyl alcohol, and the formic acid was titrated with standard base (KOH) to a phenolphthalein end point.

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CHAPTER 3

RESULTS AND DISCUSSION

THERMOLYSIS AND PHOTOLYSIS OF tert-BUTYL PEROXYFORMATE

Although tert-butyl peroxyformate (BUP), $H\text{-}CO_2\text{-}OC(CH_3)_3$, has been decomposed thermally,[1] ours is the first study of its photolysis.[2] tert-Butyl peroxyformate, like other peresters (and diacyl peroxides), has continuous weak absorption in the ultraviolet region beginning about 3200 Å; this absorption is due to an n-π^* carbonyl transition and the O-O (peroxide) group continuum.[3,4] The products from a typical photolysis experiment are shown in Table I. The results obtained by Pincock[1] from thermal decomposition are included for comparison. Theoretically the sum of the yields of carbon dioxide and formic acid should total 1.00 mole per mole of BUP decomposed, as should the sum of the yields of tert-butyl alcohol and acetone (or methane). We can account for 97% of the HCO_2- moieties and 96-99% of the $-OC(CH_3)_3$ fragments. In the case of thermolysis[1] the corresponding values are 82% and 106-108%. In a comparison of the products arising from BUP decomposition by photolysis and thermolysis, the biggest difference is in hydrogen gas yield. Whereas Pincock[1] reports that "no hydrogen is present in the product gases," we find about one-half mole of H_2 per mole of perester decomposed.

Sheldon and Kochi[4a] have reported that in the photolysis of peresters of the type $R\text{-}CO_3R'$, where R and R' are alkyl groups, the quantum yield for carbon dioxide formation is one. This observation indicates that the primary step involves two-bond homolysis (eq 1). However, it is not possible to rule out a mechanism in which the

Table I. Products of Decomposition of tert-Butyl Peroxyformate[a]

Product	Photolysis[b]	Thermolysis[c]
Hydrogen	0.46	0.00
Carbon dioxide	0.93	0.68
Formic acid	0.04	0.14
tert-Butyl alcohol	0.90	0.88
Acetone	0.09	0.18
Methane	0.06	0.20

[a]In moles per mole of performate decomposed. [b][BUP] is 0.141 M in cyclohexane; photolysis was effected by 3000 Å-region lamps in a Rayonet reactor; the temperature was 40°. [c]Data of R. E. Pincock, J. Amer. Chem. Soc., 86, 1820 (1964); [BUP] is 0.366 M in cumene; the temperature was 140°.

$$R\text{-}CO_2\text{-}OR' \xrightarrow{h\nu} R\cdot + CO_2 + R'O\cdot \qquad (1)$$

initially formed acyloxy radicals undergo very rapid decarboxylation (eq 2). The quantum yield for R· is also one, but the authors report

$$R\text{-}CO_2\text{-}OR' \xrightarrow{h\nu} R\text{-}CO_2\cdot + R'O\cdot \qquad (2a)$$

$$R\text{-}CO_2\cdot \longrightarrow R\cdot + CO_2 \qquad (2b)$$

that generally less than 50% of the R· radicals react to give RH due to the fact that reactions other than hydrogen abstraction by R· are occurring; e.g., combination with R'O· to form an ether, and disproportionation with another radical to give R(-H). It is most probable that the quantum yield for H· in BUP photolysis is unity, but that the yield of H_2 is less than one as a result of competing reactions (in this case, combination with tert-butoxy and cyclohexyl radicals). Similar results have been observed in the photolysis of acyl peroxides.[4b] Another factor contributing to the diminished amount of hydrogen gas is induced decomposition[5] of BUP (eq 3).

$$X\cdot + H\text{-}CO_2\text{-}OC(CH_3)_3 \longrightarrow XH + \cdot CO_2\text{-}OC(CH_3)_3 \qquad (3)$$

Presumably the resulting radical would decarboxylate, and the yields of carbon dioxide and tert-butyl alcohol would be undiminished. If X· were the H-atom alone, then the ratio of $[H_2]/[CO_2]$ should be one. However, there are other radicals in solution (for example,

the tert-butoxy and cyclohexyl radicals), and attack on BUP by one of them effectively reduces the $[H_2]/[CO_2]$ ratio. The small amount of formic acid observed in the present work is probably a result of BUP decomposition via thermolysis during irradiation.[1]

Photolysis of BUP at 40° in deuterated solvents such as acetone-d_6, benzene-d_6, chloroform-d_1, toluene-α,α,α-d_3 and 2-methyl-2-propanethiol-d_1 gives HD (and also some H_2). Identical solutions heated to 40° for extended periods, but not photolyzed, are free of non-condensible gases. Thermal decomposition of BUP at 100° in these solvents does yield minor amounts of HD and H_2, but not enough for quantitative analysis.

BUP-DEUTERATED THIOL SYSTEM

The photolysis of a solution containing BUP, a deuterated compound RD as a standard reactant, and a hydrogen donor QH gives H_2 and HD by the following reactions.

$$\text{BUP} \xrightarrow{h\nu} \text{H}\cdot + \text{other products} \qquad (4)$$

$$\text{H}\cdot + \text{BUP} \longrightarrow H_2 + \cdot\text{BUP} \qquad (5)$$

$$\text{H}\cdot + \text{QH} \xrightarrow{k_H} H_2 + \text{Q}\cdot \qquad (6)$$

$$\text{H}\cdot + \text{RD} \xrightarrow{k_7} H_2 + \cdot\text{RD} \qquad (7)$$

$$\text{H}\cdot + \text{RD} \xrightarrow{k_8} \text{HD} + \text{R}\cdot \qquad (8)$$

where ·BUP and ·RD are the radicals which result when a hydrogen atom is abstracted from BUP and RD, respectively, and the other symbols have their usual meaning. Although the initially formed hydrogen atom would have some excess kinetic energy, presumably it becomes thermalized very rapidly.[6]

Attack on BUP (eq 5) can be studied by observing the change of the $[H_2]/[HD]$ ratio with variation of the concentration of BUP at a constant $[QH]/[RD]$ ratio. This attack becomes important for concentrations of BUP greater than 0.03 M in cyclohexane in which a small amount of 2-methyl-2-propanethiol-d_1 ($[QH]/[RD] = 20$) is present as a deuterium donor. When the thiol concentration is increased to $[QH] = [RD]$, however, attack on BUP by the hydrogen atom remains unimportant up to 0.3 M BUP. It is most likely that abstraction from BUP occurs predominantly at the formyl moiety, since the rate constant for abstraction of an aldehyde-type hydrogen by a hydrogen atom is 10^2-10^3 times larger than that from a tert-butyl substituent.[7] This mode of induced decomposition of BUP is unique for peresters or peroxides.

Kinetic analysis of eqs 6-8 leads to eq 9. Step 5 has been

$$\frac{[H_2]}{[HD]} = \frac{k_T}{k_S} + \frac{k_H}{k_S}\frac{[QH]}{[RD]} \qquad (9)$$

omitted in this analysis since its contribution to hydrogen formation is negligible for $[BUP] = 0.02$ M, the concentration used in the runs from which relative k_H values were obtained. Thus a plot

of $[H_2]/[HD]$ against $[QH]/[RD]$ should give a straight line with a slope of k_H/k_8 and an intercept of k_7/k_8. We found that a linear relationship existed over a $[QH]/[RD]$ range of 0-18 for all compounds studied (see Table II and Figures 1-3). Linearity, of course, is a necessary but not sufficient condition that must be met if the proposed mechanism is valid.

In the kinetic runs 2-methyl-2-propanethiol-$\underline{d}_1$ was used as the standard reactant RD, since thiols can be deuterated easily by exchange with D_2O to give a very reactive deuterium donor. It should be pointed out that the easy deuteration of thiols can be a disadvantage as well in that QH compounds with exchangeable hydrogens must be deuterated also to prevent dilution of the deuterium in the thiol. In theory any donor with suitably reactive deuteriums could be used. Various other deuterated solvents (e.g., benzene-$\underline{d}_6$, acetone-$\underline{d}_6$, chloroform-$\underline{d}_1$, and toluene-$\underline{\alpha},\underline{\alpha},\underline{\alpha}$-$\underline{d}_3$) were tested for use as the standard reactant RD, but none was sufficiently reactive as a deuterium donor. The runs were made in Pyrex ampoules, and 3000 Å-region lamps were used for irradiation; under these conditions photolysis of thiol-$\underline{d}$ to give D_2 (and some HD and H_2) was negligible.[8]

Table III shows a comparison of our results with those obtained by other methods.[9a-c] The agreement is generally good, with the exception of the radiolysis values for ethyl and isopropyl alcohols. This discrepancy was previously mentioned (see Part II, Chapter 1) in connection with the discussion of the thiol systems as a source of hydrogen atoms. It would appear that the radiolysis values for

Table II. Relative Reactivities of Alkanes, Alcohols and Ethers Toward the Hydrogen Atom

QH	[QH]/[tert-BuSD]	$[H_2]/[HD]$	Relative Reactivity
Hexane	0	0.142	(1)
	1.13	0.179	
	2.09	0.217	
	3.70	0.281	
	6.03	0.360	
	8.14	0.466	
	10.2	0.504	
	12.3	0.603	
	14.5	0.669	
	16.2	0.774	
	17.6	0.805	
Cyclohexane	2.86	0.299	1.4
	5.71	0.428	
	8.50	0.601	
	11.2	0.714	
	13.9	0.898	
	16.8	1.02	
2,3-Dimethylbutane	2.42	0.311	2.1
	5.36	0.528	
	8.73	0.829	
	12.8	1.18	
	17.1	1.48	
Dodecane	3.10	0.444	2.6
	6.32	0.756	
	11.3	1.29	
	17.5	1.84	
tert-Butyl alcohol	2.94	0.146	0.05
	6.12	0.154	
	9.58	0.153	
	13.0	0.172	
	17.3	0.178	
Methyl alcohol	2.16	0.160	0.34
	4.68	0.208	
	7.65	0.221	
	10.7	0.284	
	13.6	0.300	
	17.1	0.354	

Table II, continued.

QH	[QH]/[tert-BuSD]	$[H_2]/[HD]$	Relative Reactivity
Ethyl alcohol	2.50	0.259	1.4
	5.81	0.426	
	9.64	0.651	
	12.7	0.798	
	16.7	1.03	
Isopropyl alcohol	1.83	0.329	2.6
	4.62	0.568	
	7.60	0.904	
	10.6	1.16	
	13.4	1.43	
	17.2	1.85	
p-Dioxane	2.61	0.346	2.2
	5.89	0.648	
	9.44	0.922	
	12.4	1.16	
	16.8	1.54	
Diisopropyl ether	2.33	0.562	4.9
	5.19	1.06	
	8.19	1.73	
	12.5	2.36	
	17.6	3.50	
Tetrahydrofuran	1.57	0.608	8.2
	3.61	1.24	
	5.97	1.98	
	8.22	2.76	
	10.8	3.44	
	14.0	4.50	

Figure 1. Plot of Eq 9 for the Alkane Series

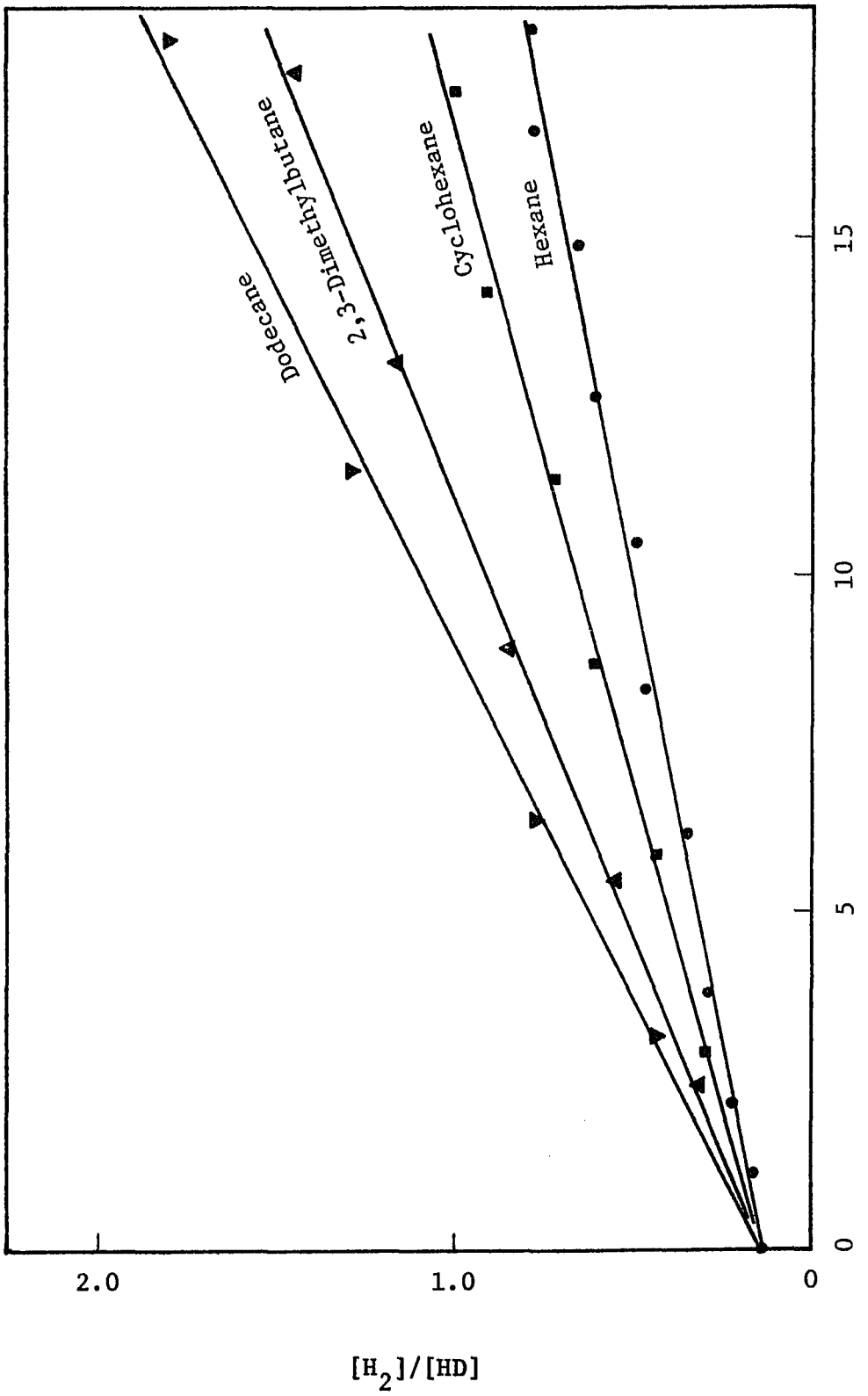


Figure 2. Plot of Eq 9 for the Alcohol Series

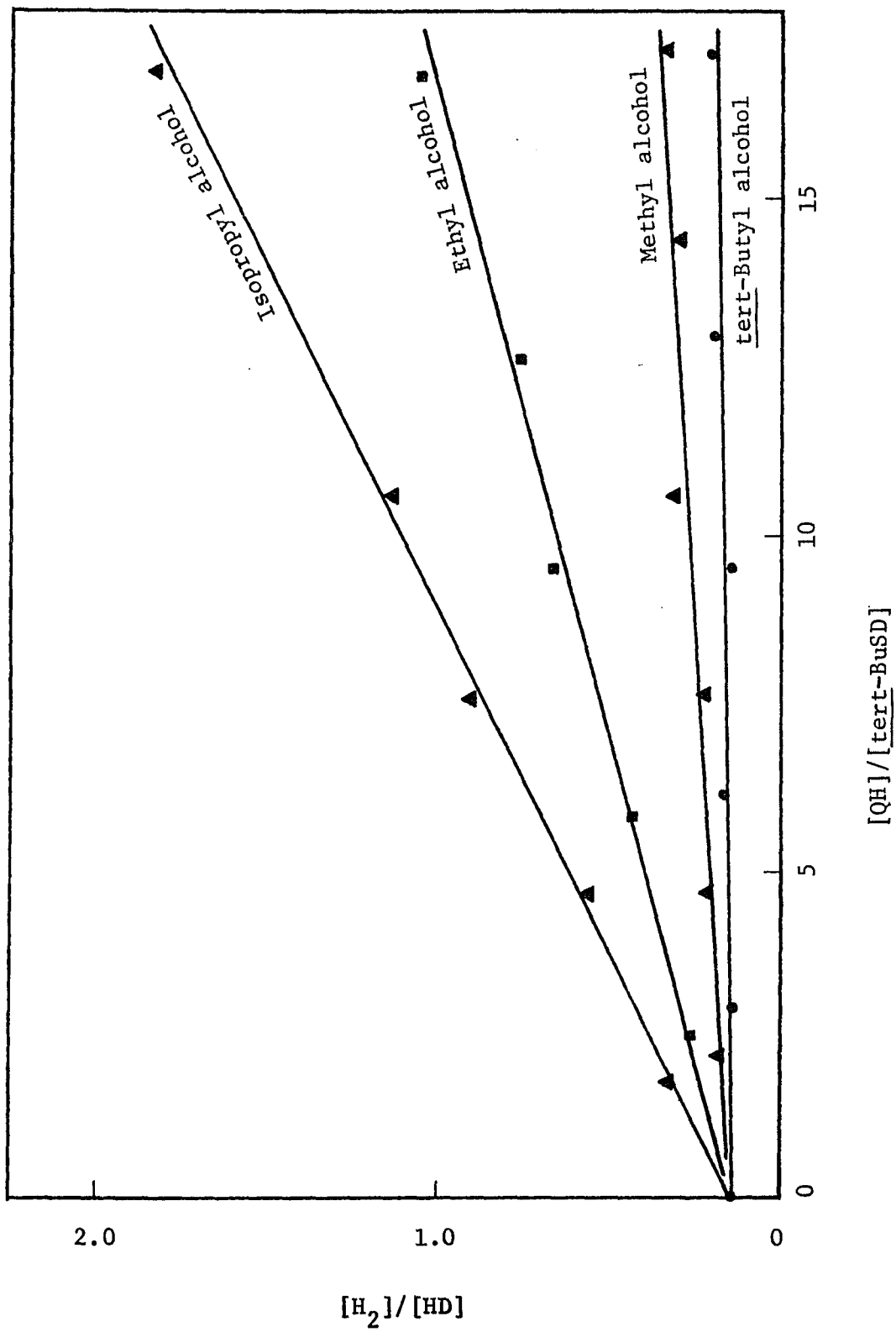


Figure 3. Plot of Eq 3 for the Ether Series

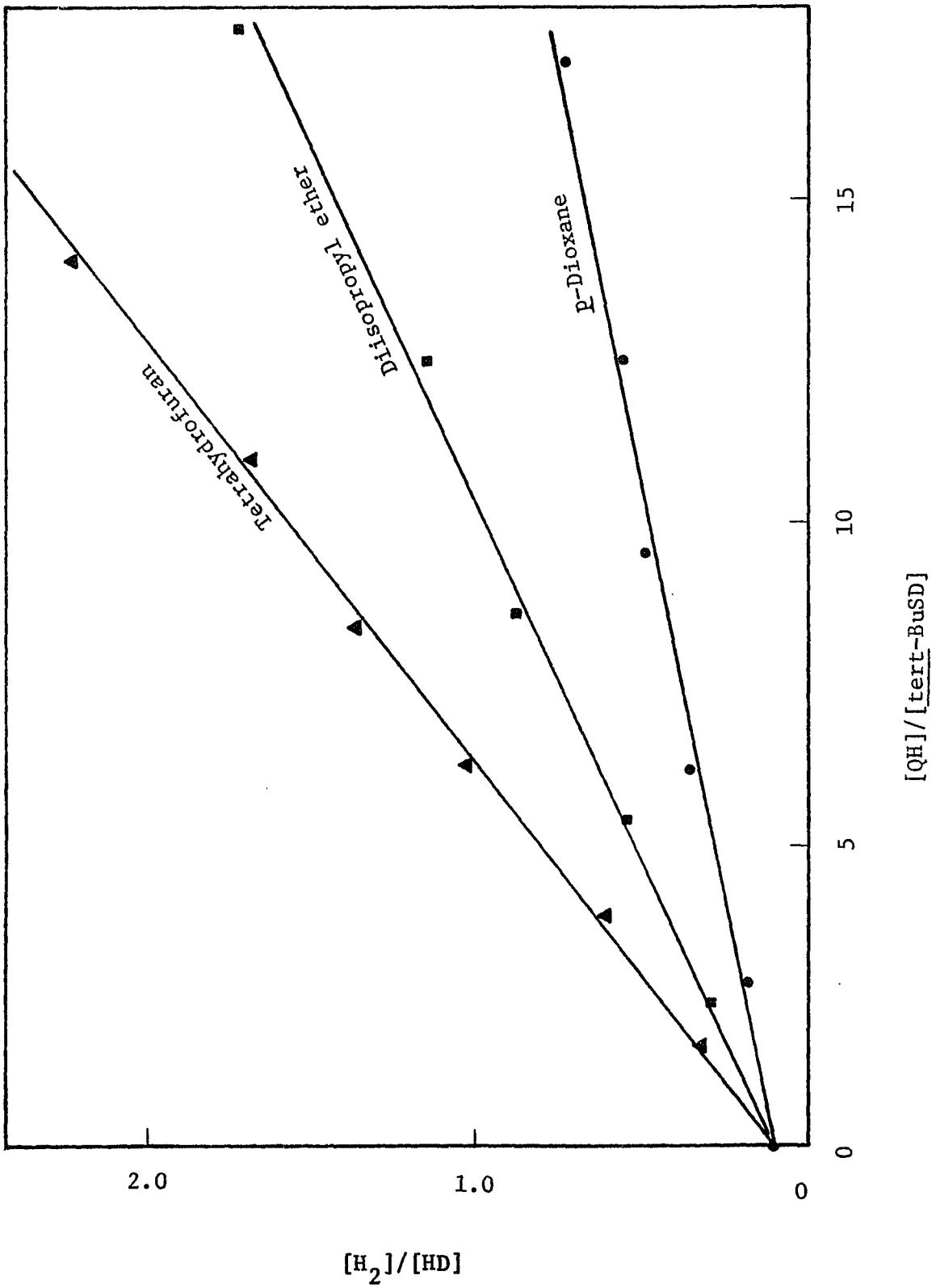


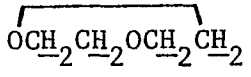
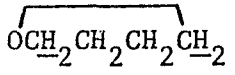
Table III. Relative Values of k_H in Eq 6 for Various Hydrogen Donors

	System			
QH	BUP	Thiol-d[a]	Thiol-t[b]	Radiolysis[c]
Hexane	(1)	(1)	(1)	(1)
Dodecane	2.6	2.3	2.0	-
Cyclohexane	1.4	1.2	1.1	1.4
2,3-Dimethylbutane	2.1	2.2	2.1	3.2
tert-Butyl alcohol	0.05	0.03	0.1	0.03
Methyl alcohol	0.34	0.42	0.43	0.42
Ethyl alcohol	1.4	1.2	0.86	4.2
Isopropyl alcohol	2.6	1.9	1.8	13.0
p-Dioxane	2.2	3.0	1.2	1.4
Diisopropyl ether	4.9	4.8	2.1	-
Tetrahydrofuran	8.2	9.1	-	7.7

[a]Either 2-methyl-2-propanethiol-d or thiophenol-d gives the same value; data of W.A. Pryor, J. P. Stanley and M. Griffith, Science, 169, 181 (1970). [b]Thiophenol-t was used; see W. A. Pryor, T. H. Lin and J. P. Stanley, in preparation. [c]Taken from a compilation of data in W. A. Pryor and J. P. Stanley, J. Amer. Chem. Soc., 93, in press.

ethyl and isopropyl alcohol are not artifacts, since they have been reproduced in several different laboratories. However, we feel that there is strong evidence that the results from the BUP and thiol systems may be correct and the radiolysis values incorrect. This argument is based on the internal consistency of the data. As Table IV shows, the $1^{o}:2^{o}$ reactivity ratio for hydrogens $\underline{\alpha}$ to an oxygen is $1:\sim3$, with the exception of the values for tetrahydrofuran as measured by all methods and the radiolysis value for ethyl alcohol. Similarly, the $1^{o}:3^{o}$ selectivity is about 1:16, with the exception of the radiolysis value for isopropyl alcohol, in which case the ratio is 1:92. The value of 92 appears to be unreasonably large, and if omitted, a selectivity of $1^{o}:3^{o} = 1:\sim16$ is obtained.[9d] Turning again to the $1^{o}:2^{o}$ selectivity, we see that a ratio of $1:\sim15$ is untenable, if the $1^{o}:3^{o}$ ratio is $1:\sim16$. On the other hand, $1^{o}:2^{o} = 1:\sim3$ is quite reasonable. The selectivity profile $1^{o}:2^{o}:3^{o} = 1:\sim3:\sim16$ is internally consistent with the majority of data, and it appears that the enhanced reactivities of tetrahydrofuran (from the three systems) and of ethyl and isopropyl alcohols (from radiolysis) are spuriously large. It is tempting, perhaps, to attempt to rationalize the high value for tetrahydrofuran on the basis that the hydrogens $\underline{\beta}$ to the oxygen contribute appreciably to the overall reactivity. It is unlikely that reaction with the $\underline{\beta}$-hydrogens is important, since the presence of an oxygen activates an $\underline{\alpha}$-hydrogen by a factor of 5-10 (compared to the reactivity of a hydrogen $\underline{\alpha}$ to a carbon), but apparently does not enhance the $\underline{\beta}$-hydrogen reactivity to any great extent.[9a] Also, it is not possible to explain the

Table IV. Comparison of the Relative Reactivities of Alcohols and Ethers Toward the Hydrogen Atom

QH[a]	System			
	BUP	Thiol-d[b]	Thiol-t[c]	Radiolysis[d]
	primary hydrogen α to an oxygen[e]			
CH_3OH	(1)	(1)	(1)	(1)
	secondary hydrogen α to an oxygen[e]			
$HOCH_2CH_2OH$	-	-	-	3.8
	2.0	2.7	1.1	1.2
CH_3CH_2OH	4.9	4.2	3.0	14.3
	14.8	16.5	-	14.0
	tertiary hydrogen α to an oxygen[e]			
$(CH_3)_2CHOH$	19.3	14.1	13.3	92.0
$[(CH_3)_2CH]_2O$	17.7	17.4	-	-
$(HOCH_2)_2CHOH$	-	-	-	17.0
$HOCH_2(CHOH)_4CHO$	-	-	-	15.8

[a]Only the hydrogens underlined are assumed to contribute significantly to the overall reactivity. [b]W. A. Pryor and J. P. Stanley, J. Amer. Chem. Soc., 93, in press. [c]W. A. Pryor, T. H. Lin and J. P. Stanley, in preparation. [d]Taken from a review by M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotop., 18, 493 (1967). [e]On a per hydrogen basis.

tetrahydrofuran results in terms of ring size, since the reactivity of cyclopentane is not significantly greater than that of hexane, pentane or cyclohexane.[9a,9c]

BUP-BENZENE SYSTEM

The reasonableness and agreement of our results with those obtained by other methods does not, of course, prove the presence of hydrogen atoms in our system, although this interpretation is clearly the simplest and most attractive. Other suggestions could be made to explain the formation of hydrogen gas. For example, it is possible that an as yet unknown type of photolytic interaction between the thiol and BUP could be responsible for some of the H_2 or HD.[10] To test this hypothesis we developed a thiol-free perester-benzene system. The pertinent reactions are given in eqs 10-13.

$$\text{BUP} \xrightarrow{h\nu} \text{H}\cdot + \text{other products} \qquad (10)$$

$$\text{H}\cdot + \text{QH} \xrightarrow{k_H} \text{H}_2 + \text{Q}\cdot \qquad (11)$$

$$\text{H}\cdot + \text{PhH} \xrightarrow{k_{12}} \text{H}_2 + \text{Ph}\cdot \qquad (12)$$

$$\text{H}\cdot + \text{PhH} \xrightarrow{k_{13}} \text{PhH}_2\cdot \qquad (13)$$

where $PhH_2\cdot$ is the radical resulting when a hydrogen atom adds to the benzene ring, and the other symbols have their usual meaning. This system involves a competition between QH and benzene for hydrogen atoms. The rate of hydrogen gas formation is given in eq 14.

$$\frac{d[H_2]}{dt} = [H\cdot](k_H[QH] + k_{13}[PhH]) \qquad (14)$$

If ΦI is the rate of formation of hydrogen atoms, then steady state treatment in H-atoms gives eq 15. Substitution of eq 15 into eq 14

$$[H\cdot] = \frac{\Phi I}{k_H[QH] + k_{13}[PhH]} \qquad (15)$$

gives eq 16. Since k_{13} is 10-10^3 times larger than k_H,[12] then

$$\frac{d[H_2]}{dt} = \Phi I \frac{k_H[QH] + k_{12}[PhH]}{k_H[QH] + k_{13}[PhH]} \qquad (16)$$

for $[QH] \leq [PhH]$, eq 16 becomes

$$\frac{1}{\Phi I}\frac{[H_2]}{dt} = \frac{k_{12}}{k_{13}} + \frac{k_H}{k_{13}}\frac{[QH]}{[PhH]} \qquad (17)$$

Integration of eq 17 (assuming low conversions) gives eq 18.

$$\frac{[H_2]}{\Phi I_t} = \frac{k_{12}}{k_{13}} + \frac{k_H}{k_{13}}\frac{[QH]}{[PhH]} \qquad (18)$$

where $I_t = \int_0^t I dt$, i.e., the total amount of light absorbed by the sample. In practice, $[H_2]/\Phi I_t$ was assigned an arbitrary value of one for $[QH]/[PhH] = 0$; in this way the stability of the lamps was removed as a variable. Thus a plot of relative H_2 yield against

[QH]/[PhH] should give a line with a slope that is proportional to k_H. However, curvature in the line should appear when [QH] > [PhH]. This deviation in linearity is expected, since the factor k_H[QH] in the denominator on the right hand side of eq 16 becomes important, thereby eliminating use of the simplification necessary to obtain eqs 17 and 18.

The samples were irradiated for an hour, and the relative hydrogen yields were determined by mass spectrometry. Table V gives the data, and Figure 4 shows a plot of relative hydrogen yield vs. [Hexane]/[PhH] over the entire range from neat benzene to essentially neat hexane. Initially the slope is constant, but for [Hexane]/[PhH] > 2, curvature becomes apparent. The relative reactivities of representative hydrogen donors were determined using the BUP-benzene system; the results are shown in Table VI and Figure 5.

A comparison of the results from the BUP-benzene system with those from the BUP-thiol-d system is given in Table VII. The agreement is rather good over a 10^2 range of reactivities, the only exception being the value for tetrahydrofuran. As was discussed earlier in this chapter, the reactivity of tetrahydrofuran as measured by the other methods is considerably larger than that predicted for a compound having four hydrogens α to an oxygen. The value determined in the BUP-benzene system is much more reasonable, giving a per hydrogen reactivity of 4.2 compared to a methyl-hydrogen in methyl alcohol (see Table IV).

That the hydroxyl hydrogens in the alcohols are unreactive toward the hydrogen atom was demonstrated by two control

Table V. Relative H_2 Yields for Various Ratios of [Hexane]/[PhH] in the BUP-Benzene System

No.	[Hexane]/[PhH]	Relative H_2 Yield
1	0	(1)
2	0.062	1.10
3	0.141	1.33
4	0.226	1.42
5	0.391	1.66
6	0.458	1.91
7	0.575	2.03
8	0.680	2.24
9	0.680	2.32
10	0.841	2.61
11	0.927	2.73
12	1.14	3.05
13	4.25	7.43
14	10.1	10.6
15	10.1	11.2
16	26.4	14.3
17	26.4	14.7
18	53.8	19.8
19	53.8	20.5
20	128.	23.5
21	128.	23.9

Figure 4. Relative H_2 Yield vs. [Hexane]/[PhH]

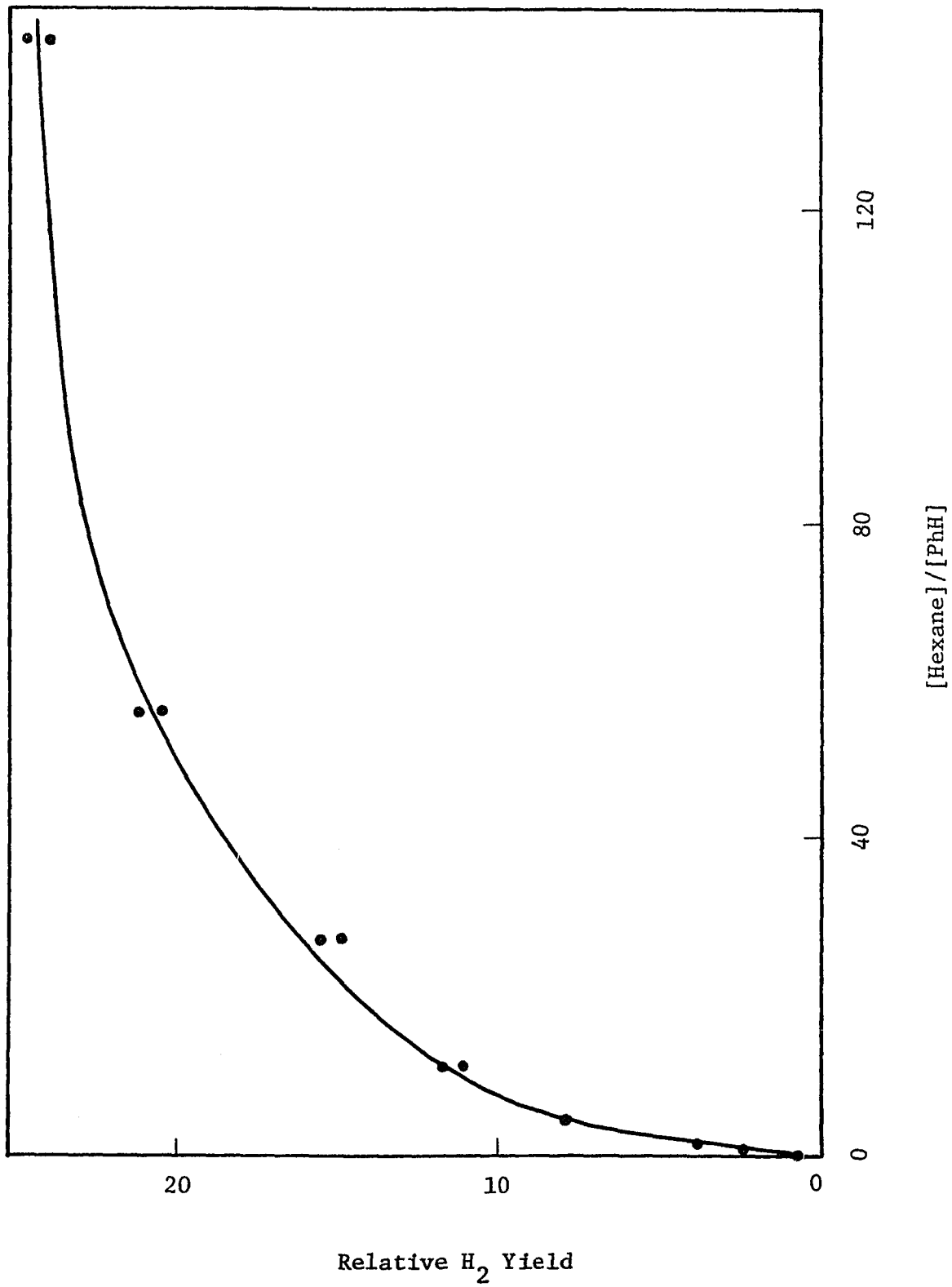


Table VI. Relative H_2 Yields for Various Ratios of [QH]/[PhH]

QH	[QH]/[PhH]	Relative H_2 Yield[a]	Relative Slope[b]
tert-Butyl alcohol	0.190	0.99	0.03
	0.292	1.06	
	0.388	1.03	
	0.560	1.04	
	0.667	1.08	
	0.818	1.11	
Methyl alcohol	0.163	1.12	0.39
	0.331	1.26	
	0.548	1.37	
	0.687	1.46	
	0.790	1.59	
Ethyl alcohol	0.117	1.30	1.5
	0.283	1.82	
	0.522	2.43	
	0.614	2.76	
	0.726	3.01	
Tetrahydrofuran	0.133	1.51	2.2
	0.226	1.94	
	0.299	2.33	
	0.396	2.53	
	0.490	3.03	
	0.596	3.32	
2,3-Dimethylbutane	0.155	1.62	2.4
	0.288	2.31	
	0.424	2.92	
	0.577	3.50	
Isopropyl alcohol	0.080	1.42	2.8
	0.178	1.97	
	0.315	2.62	
	0.393	3.02	
	0.454	3.43	

[a]The H_2 yield in neat benzene is set equal to one. [b]The slope for hexane is set equal to one.

Figure 5. Relative H_2 Yields vs. [QH]/[PhH] for Various Hydrogen Donors QH

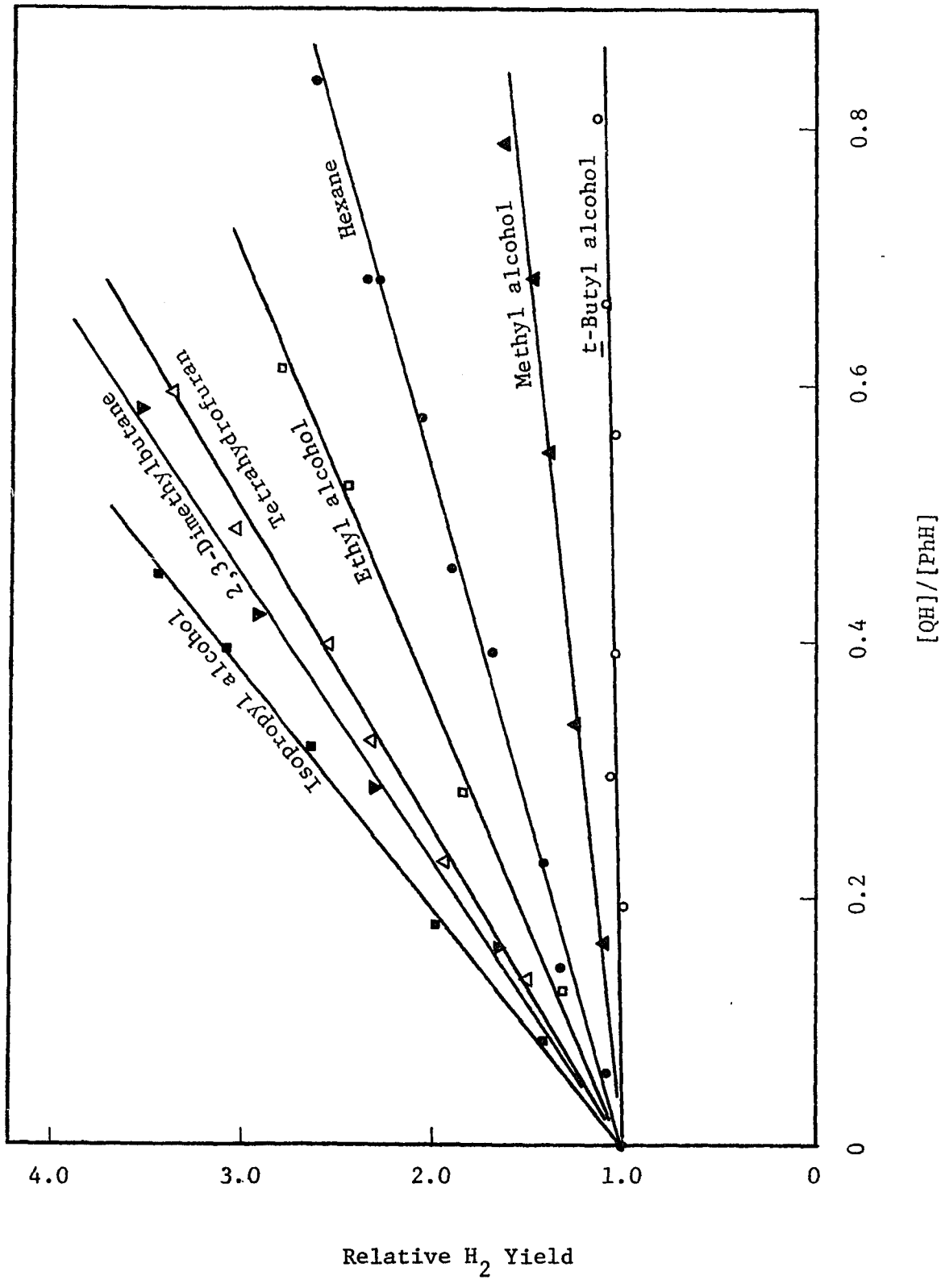


Table VII. Relative Values of k_H in Eq 6 for Various Hydrogen Donors

	System	
QH	BUP-Benzene	BUP-Thiol-*d*
Hexane	(1)	(1)
tert-Butyl alcohol	0.03	0.05
Methyl alcohol	0.39	0.34
Ethyl alcohol	1.5	1.4
Isopropyl alcohol	2.8	2.6
2,3-Dimethylbutane	2.4	2.1
Tetrahydrofuran	2.2	8.2

experiments. In the first, BUP was photolyzed in alcohol-d, and the non-condensible gas was checked for HD. None was found, indicating that either the hydroxyl hydrogen is unreactive, or that there is a very large deuterium isotope effect on the abstraction. In the second and more conclusive experiment, the reactivity of alcohol-d was found to be identical with that of alcohol. These controls show that the reactivity of an alcohol toward the hydrogen atom is due entirely to the alkyl group.[14]

A source of concern in the BUP-benzene system is the fate of the cyclohexadienyl radicals formed by addition of hydrogen atoms to benzene. In order for the kinetic equation (eq 18) to be valid, it is necessary that the reaction of H-atoms with either the cyclohexadienyl radical or its dimer, dihydrobiphenyl (a very good hydrogen donor), be unimportant. As a test for the contribution of the first possibility the light flux on the samples was varied over a range of about 20. Higher radical concentrations would be associated with a higher flux, and the hydrogen atom-cyclohexadienyl radical reaction should be more important. However, light flux did not affect the results. The second possibility, reaction of the H-atom with dihydrobiphenyl, was probed by varying the conversion of reaction. Again, no difference was noted over a five-fold change in extent of conversion. Nevertheless, possible complications were minimized by keeping the conversion in kinetic runs to less than 0.5%.

The results from the BUP-benzene system indicate that photolytic interaction between BUP and thiol is not a viable alternative. The reactivity of tetrahydrofuran observed in this system is much

lower than that previously reported. The reason for this discrepancy is not obvious. One suggestion might be that some adventitious hydrogen donor is formed from a molecule of tetrahydrofuran that has lost a hydrogen atom. This donor is scavenged by benzene in the BUP-benzene system, but reacts with H-atoms in the other systems. This possibility is unlikely since conversions in the BUP-thiol-d system were kept to less than 0.5%; for this donor to compete successfully with its parent compound(tetrahydrofuran), it would have to be reactive enough to overcome a minimum concentration deficit of more than 100. No organic hydrogen donor measured to date even approaches this value. At present there does not appear to be an entirely satisfactory explanation for the disagreement.

Russell[15] found the chlorine atom to be more selective in solvents that complex this radical (e.g., benzene and carbon disulfide) than in carbon tetrachloride, a non-complexing solvent. Our results, though not definitive, indicate that such behavior may be found in the reactions of the hydrogen atom as well, though the effect is much less pronounced than for the chlorine atom.

RHO-VALUE FOR HYDROGEN ABSTRACTION FROM SUBSTITUTED TOLUENES

Another suggestion to explain the H_2 and HD formation in the photolysis of BUP in a solution of QH and RD is that a photoexcited BUP species abstracts H(D) atoms from QH(RD) and then eliminates H_2(HD). Hydrogen abstraction by photoexcited carbonyl groups is well known;[3,16-21] however, this mechanism is contraindicated by the fact that formic acid, oxalic acid and ethyl formate all fail to give H_2 upon irradiation under the conditions used to photolyze

BUP. Also, as was pointed out earlier in this chapter, Sheldon and Kochi[4a] have found that peresters of the type RCO_3R', where R is an alkyl group, give R· when photolyzed; the photolysis of $H\text{-}CO_2\text{-}OC(CH_3)_3$ to give H· and $R\text{-}CO_2\text{-}OC(CH_3)_3$ to give R· seems quite analogous. In an attempt to elucidate the mechanism of formation of H_2 arising from the photolysis of BUP (that is, whether hydrogen is abstracted by the H-atom or photoexcited perester), we undertook a study of the polarity of the abstracting species.

Using meta- and para-substituted toluenes as substrates, Walling and Gibian[22] studied the sensitivity of triplet benzophenone toward electron availability, and found a quite large negative Hammett ρ-value for hydrogen abstraction by the triplet (see Table VIII). The ketone triplet and an alkoxy radical are similar both thermochemically and electronically,[22] and they should behave similarly. As Table VIII shows, the ρ-values for the ketone triplet and the tert-butoxy radical are both appreciably negative; that is, these radicals are quite electrophilic. On the other hand, the methyl and phenyl radicals, which should serve as good models for estimation of the polarity of the hydrogen atom, are considerably more electroneutral, as evidenced by their small, negative ρ-values. If photoexcited perester is important in H_2 formation, it would be expected that the ρ-value for hydrogen abstraction from substituted toluenes would be on the order of -1, whereas if the H-atom is the abstracting species a ρ-value much smaller (-0.1 to -0.2) should be observed.

Using the BUP-thiol-d system, we determined the relative reactivities of various substituted toluenes. The data are shown in Table IX and plotted in Figures 6-10, and a summary of the results

Table VIII. ρ-Values for Attack by Radicals on Substituted Toluenes

Radical	ρ-Value[a]	Reference
tert-BuO·	-0.68	b
tert-BuO·	-0.60	c
tert-BuO·	-0.83	d
$Ph_2\dot{C}$-$\dot{O}$	-1.16	e
Me·	-0.14	f
Ph·	-0.1	g

[a]The correlation is with σ^+ substituent constants.

[b]B. Kennedy and K. U. Ingold, Can. J. Chem., 44, 2381 (1966). [c]R. Gilliom and B. Ward, Jr., J. Amer. Chem. Soc., 87, 3944 (1965). [d]C.Walling and B. B. Jacknow, ibid., 82, 6113 (1960). [e]C. Walling and M. Gibian, ibid., 87, 3361 (1965). [f]W. A. Pryor, U. Tonellato, D. Fuller and S. Jumonville, J. Org. Chem., 34, 2018 (1969). [g]R. F. Bridger and G. A. Russell, J. Amer. Chem. Soc., 85, 3754 (1963).

Table IX. Reactivities of Substituted Benzenes and Toluenes Toward the Hydrogen Atom

QH	[QH]/[tert-BuSD]	$[H_2]/[HD]$	Slope
Benzene	2.11	0.194	0.025
	4.66	0.239	
	7.32	0.330	
	10.2	0.393	
	13.2	0.428	
	15.8	0.522	
Toluene	2.64	0.280	0.057
	5.80	0.483	
	8.00	0.594	
	10.1	0.738	
	13.3	0.881	
	16.5	1.10	
m-Xylene	2.18	0.342	0.098
	4.69	0.601	
	7.41	0.855	
	11.0	1.24	
	15.5	1.66	
p-Xylene	2.63	0.381	0.097
	5.62	0.674	
	8.93	0.997	
	12.4	1.35	
	16.2	1.69	
tert-Butylbenzene	2.48	0.272	0.056
	5.73	0.448	
	9.96	0.730	
	13.7	0.887	
	16.4	1.05	
1-tert-Butyl-4-methylbenzene	3.21	0.398	0.089
	6.18	0.713	
	9.30	0.966	
	12.5	1.23	
	16.1	1.62	
Bromobenzene	4.55	0.250	0.029
	7.84	0.386	
	11.4	0.482	
	15.8	0.591	

Table IX, continued.

QH	[QH]/[tert-BuSD]	$[H_2]/[HD]$	Slope
3-Bromotoluene	2.89	0.286	0.057
	6.10	0.493	
	10.4	0.681	
	13.1	0.944	
	16.7	1.14	
Chlorobenzene	3.03	0.220	0.030
	6.69	0.361	
	10.1	0.433	
	13.2	0.526	
	16.5	0.638	
3-Chlorotoluene	3.16	0.328	0.062
	6.39	0.540	
	8.51	0.662	
	11.7	0.855	
	16.0	1.19	
4-Chlorotoluene	2.22	0.263	0.059
	5.40	0.458	
	8.75	0.626	
	12.4	0.872	
	15.9	1.08	
Fluorobenzene	3.29	0.221	0.028
	7.64	0.363	
	10.0	0.417	
	12.1	0.503	
	16.4	0.585	
3-Fluorotoluene	2.70	0.278	0.056
	5.84	0.482	
	9.61	0.654	
	12.7	0.839	
	16.6	1.11	

Figure 6. Plot of Eq 9 for Benzene, Toluene, and m- and p-Xylene

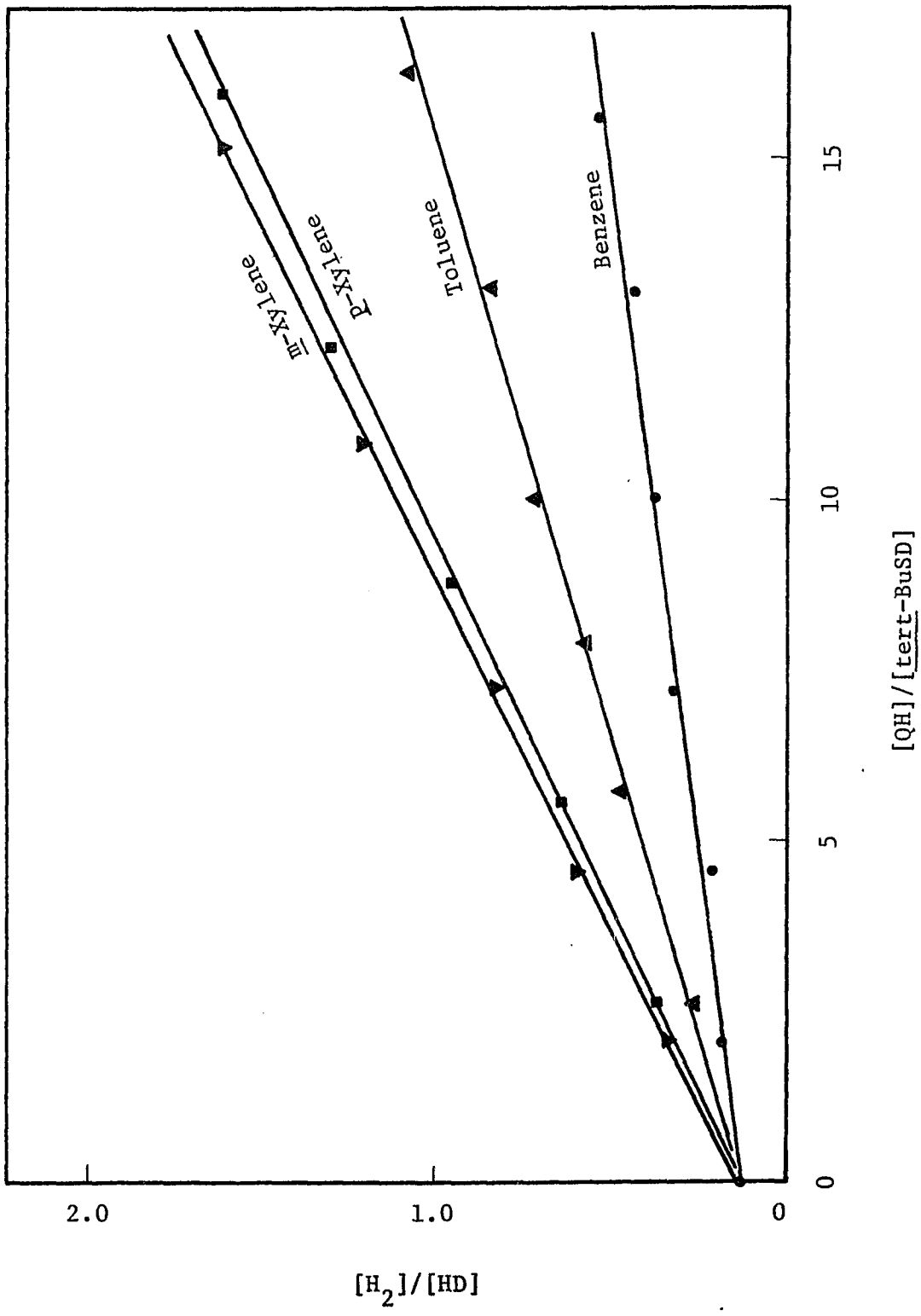


Figure 7. Plot of Eq 9 for tert-Butylbenzene and 1-tert-Butyl-4-methyltoluene

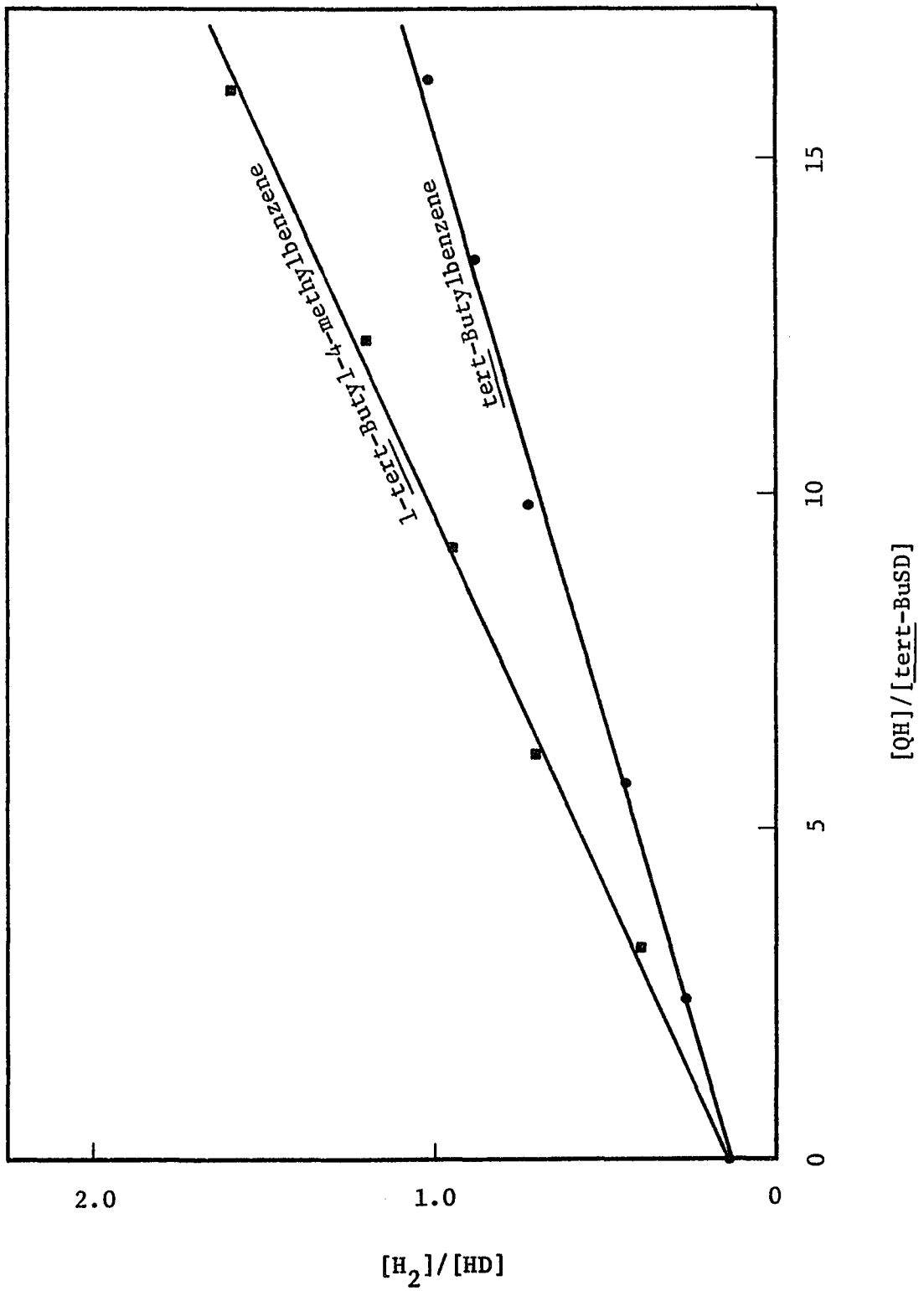
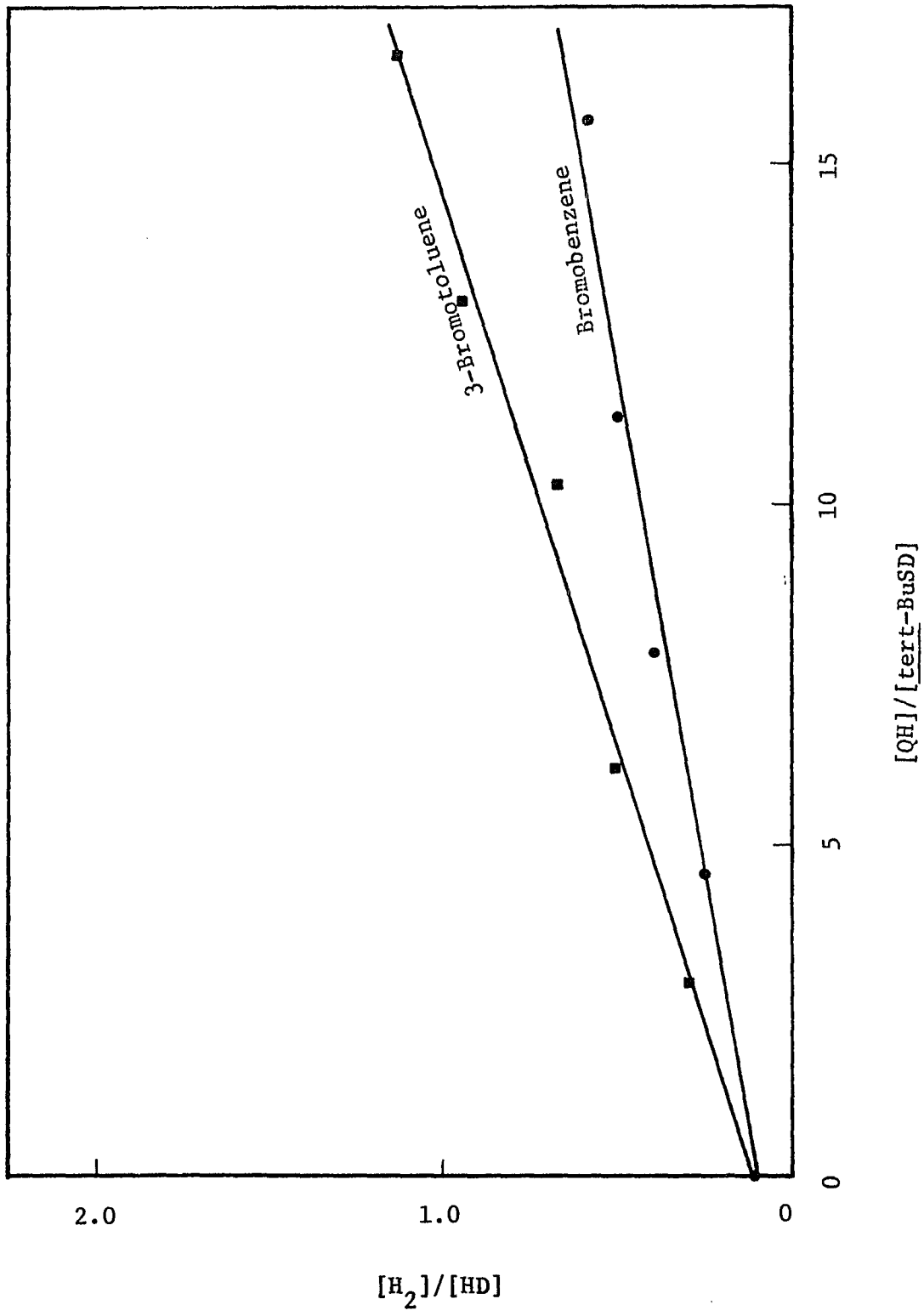


Figure 8. Plot of Eq 9 for Bromobenzene and 3-Bromotoluene



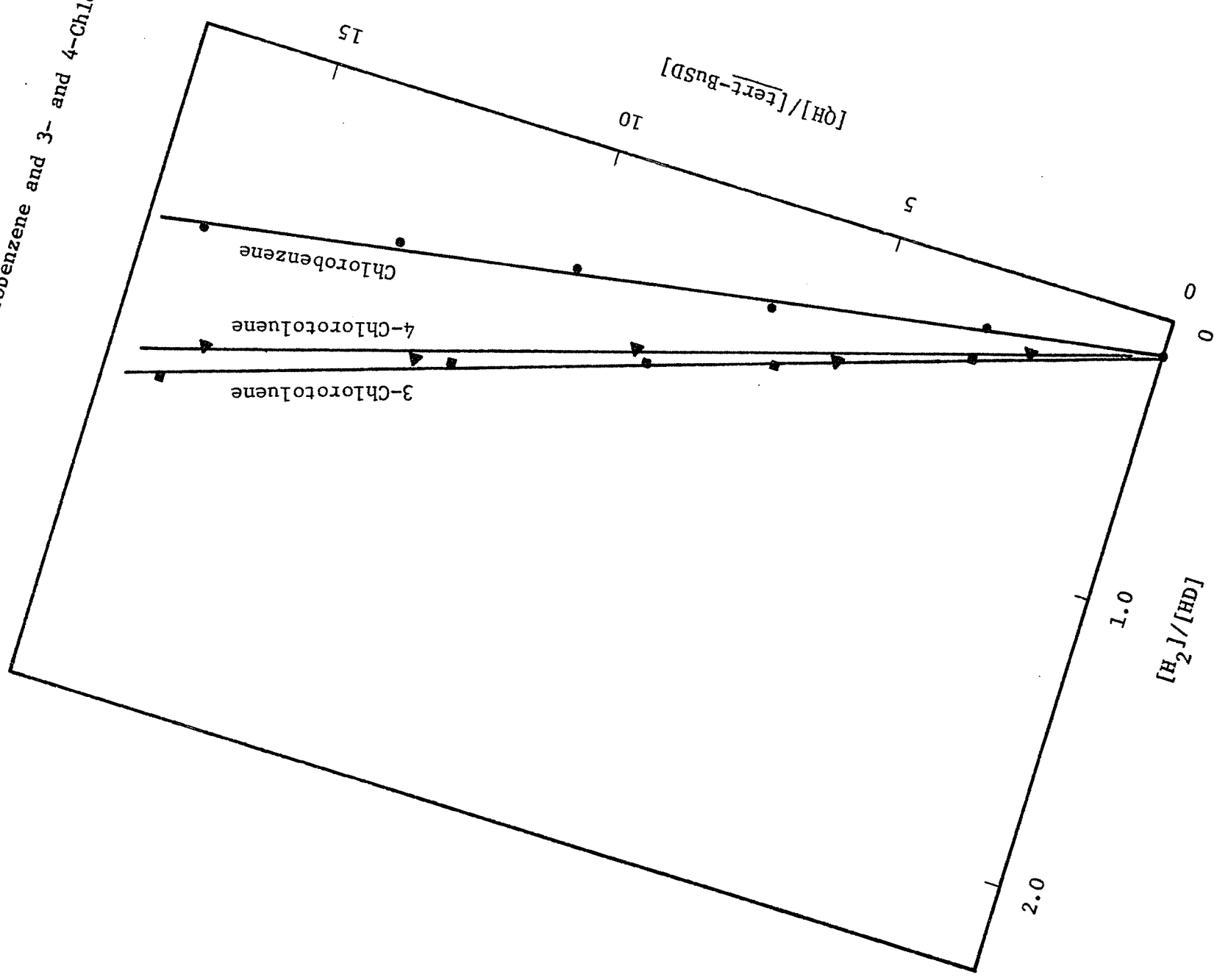


Figure 9. Plot of Eq 9 for Chlorobenzene and 3- and 4-Chlorotoluene

Figure 10. Plot of Eq 9 for Fluorobenzene and 3-Fluorotoluene

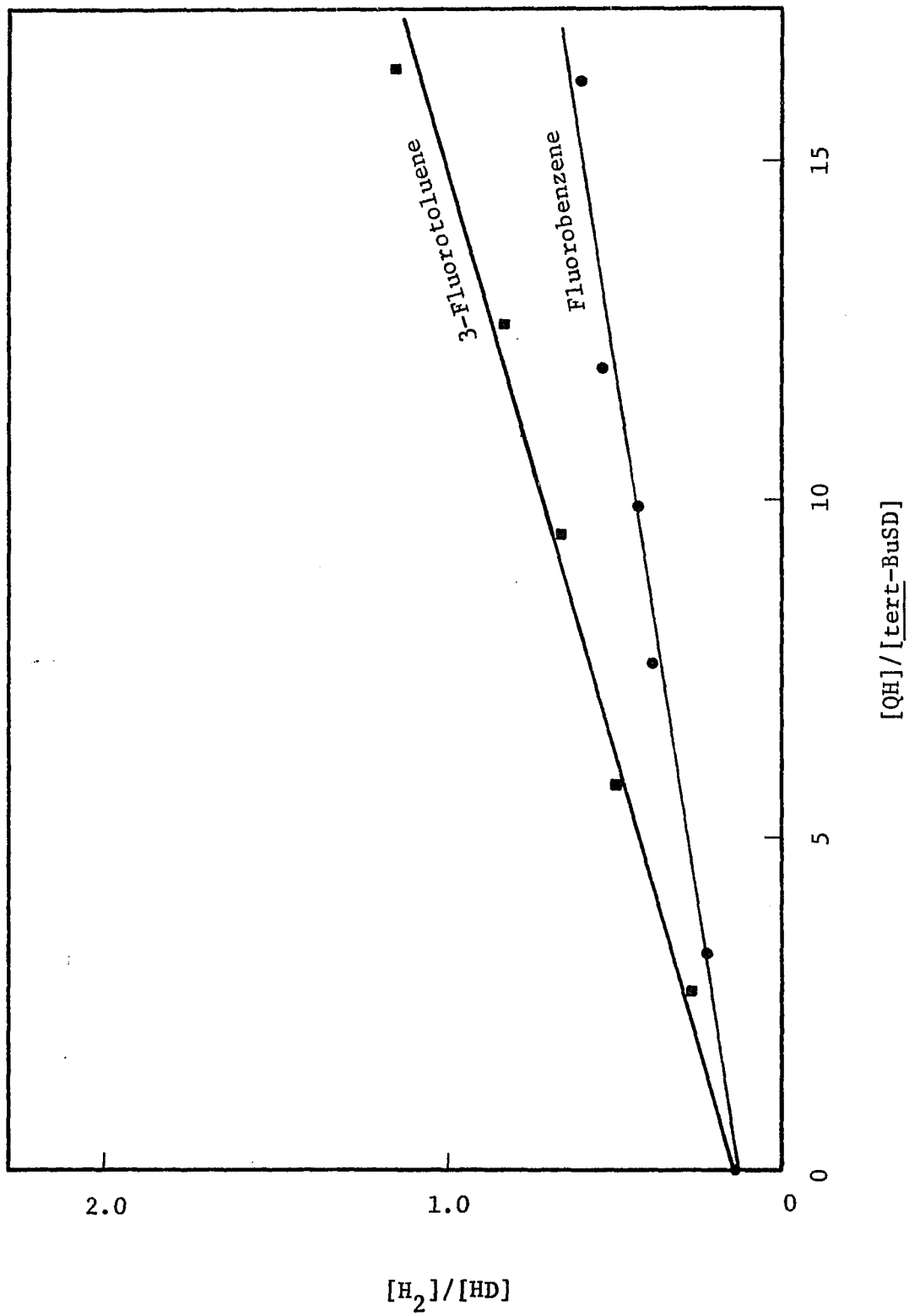


Table X. Summary of the Relative Reactivities of Substituted Benzenes and Toluenes Toward the Hydrogen Atom

R-	Slope[a] of line for R-$PhCH_3$	Slope[a] of line for R-Ph	Relative Rate[b]	σ^{+}[c]
H-	0.057	0.025	(1)	0
3-Me-	0.098	0.025[d]	1.15	-0.065
4-Me-	0.097	0.025[d]	1.12	-0.31
4-tert-Bu-	0.089	0.056	1.03	-0.25
3-Br-	0.057	0.029	0.80	0.40
3-Cl	0.062	0.030	1.00	0.39
4-Cl-	0.059	0.030	0.90	0.11
3-F-	0.056	0.028	0.86	0.35

[a]Taken from a plot of $[H_2]/[HD]$ vs. [QH]/[tert-BuSD]. [b]Obtained by subtracting the value of the slope for R-Ph from that for R-$PhCH_3$; relative to toluene on a per hydrogen basis. [c]H. C. Brown and Y. Okamoto, J. Org. Chem., 22, 485 (1957). [d]The value for benzene was used.

is given in Table X. In order to isolate the reaction of the hydrogen atom with the side chain of the substituted toluenes, a correction was made to eliminate the contribution of the ring. In each case the reactivity of R-Ph was subtracted from that of R-$PhCH_3$. The value for benzene[23] was used to correct the reactivities of the xylenes. Figure 11 shows the σ ρ plot[25a] for the BUP photolysis system. The ρ-value is -0.13 when σ^+ substituent constants[25b] are used; the correlation is poorer with σ substituent constants, but even then $\rho < -0.2$. This small, negative ρ-value is very strong evidence that the formation of H_2 is *via* the hydrogen atom and not excited perester.

Although other workers[26-28] have reported that the hydrogen atom is electrophilic, the present work is the first quantitative measurement of its electrophilicity. Anbar[26] found that the H-atom abstracts the *α*-hydrogen on the carboxylate ion faster than that on the corresponding acid. Also, Anbar, *et al.*[27] have shown that hydrogen atom addition to the aromatic ring is enhanced by electron donating substituents and retarded by electron withdrawing substituents. They obtained a ρ-value of -0.7 for such addition, but the scatter of their data is appreciable, and assignment of appropriate substituent constants is difficult. However, their basic conclusion, *i.e.*, that the H-atom is an electrophilic species, is valid. Sauer and Mani[28] studied the rate of addition of the hydrogen atom to monosubstituted benzenes, and obtained results comparable to Anbar's, concluding that the hydrogen atom is electrophilic.

In the final table, Table XI, the selectivity of the H-atom is

Figure 11. Hammett Plot for Reaction of the Hydrogen Atom with Substituted Toluenes

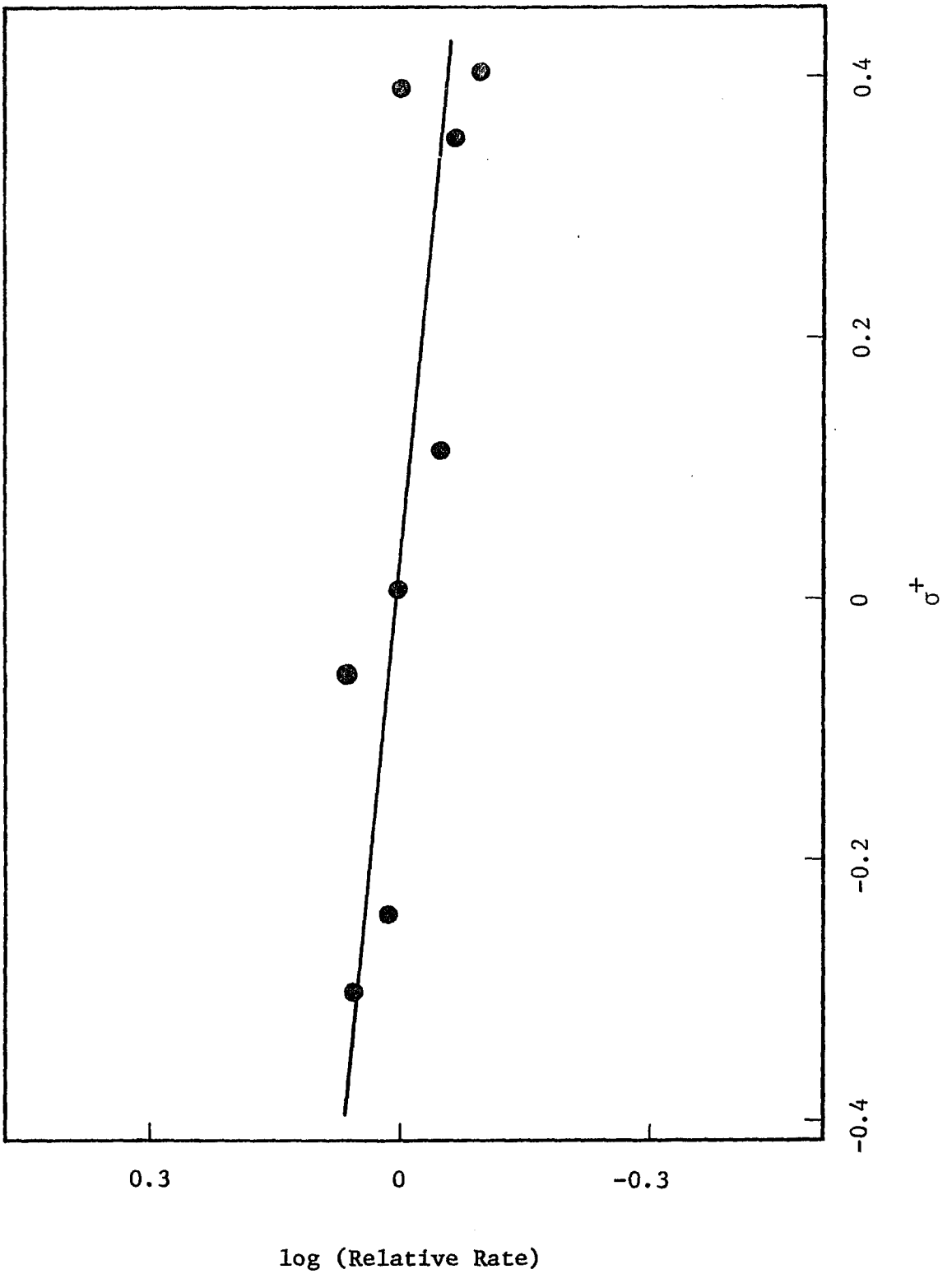


Table XI. Rate Constants for Hydrogen Abstraction from Organic Compounds by Various Radicals

Hydrogen donor	Relative Reactivities per Hydrogen				
	H·	Me·		RCH_2·[b]	Ph·[c]
	soln	gas	soln	soln	soln
Alkanes					
1° hydrogen	(1)	(1)[d]	(1)[e]	(1)	(1)
2° hydrogen	3.3	5.0[d]	4.3[e]	4.3	9.
3° hydrogen	31.	33.[d]	46.[e]	-	44.
Alcohols[f]					
$C\underline{H}_3OH$	(1)	(1)[g]	(1)[h]	(1)	-
$CH_3C\underline{H}_2OH$	4.1	4.9[g]	4.1[h]	5.	-
$(CH_3)_2C\underline{H}OH$	17.	25.[g]	46.[h]	20.	-

[a]Data of W. A. Pryor and R. W. Henderson, J. Amer. Chem. Soc., 92, 7234 (1970); see also, W. A. Pryor and J. P. Stanley, ibid., 93, in press. [b]G. A. Mortimer, J. Polym. Sci., Part A-1, 4, 881 (1966). [c]R. F. Bridger and G. A. Russell, J. Amer. Chem. Soc., 85, 3754 (1963). [d]W. M. Jackson, J. McNesby and B. deB Darwent, J. Chem. Phys., 37, 1610 (1962). [e]W. A. Pryor and D. Fuller, unpublished results. [f]Relative reactivities are for the hydrogens underlined. [g]A. A. Herrod, Chem. Commun., 891 (1968); data are for the CD_3· radical. [h]J. K. Thomas, J. Phys. Chem., 71, 1919 (1967).

compared with that of the phenyl,[29] methyl,[30] and polymethylene[31] radicals. The relative rates of abstraction of primary, secondary and tertiary hydrogens from alkanes by the various radicals are all about the same, and in the alcohol series, the same parallel is observed. This similarity in selectivity profiles probably reflects the approximately equal bond strengths of the bonds being formed, as well as the lack of appreciable polar character in the radicals.[32]

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7. (a) M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotop., 18, 493 (1967); (b) J.C.J.Thynne, Trans. Faraday Soc., 58, 676 (1962).
8. Although photolysis of thiol in Pyrex ampoules with 3600 Å-region lamps for several hours fails to give any H_2, it is still possible that some homolysis (e.g., C-S bond scission) could be occurring. As a control experiment, a solution of cyclohexane

and thiol-t was irradiated under the conditions used for kinetic runs with BUP. The recovered cyclohexane was inactive; this indicates that no radicals were produced which could lead to cyclohexyl radicals, since if cyclohexyl radicals were formed, they would react with thiol-t to give labeled cyclohexane.

9. (a) Photolysis of thiol-d: see W.A. Pryor, J.P. Stanley and M. Griffith, Science, 169, 181 (1970); W.A. Pryor and J.P. Stanley, J. Amer. Chem. Soc., 93, in press; (b) Photolysis of thiol-t: see W.A. Pryor and M. Griffith, ibid., 93, (1971); W.A. Pryor, T.H. Lin and J.P. Stanley, in preparation; (c) Radiolysis: see R.A. Holroyd, J. Phys. Chem., 70, 1341 (1966); T.J. Hardwick, ibid., 66, 2246 (1962), and previous papers in this series; reference 7a; (d) J.H. Baxendale and D.H. Smithes (Z. Phys. Chem., 7, 242 (1956)) report a $1^{o}:3^{o}$ ratio of 1:28 for methyl alcohol and isopropyl alcohol on a per hydrogen basis.

10. For an example of the interaction between a carbonyl group and a sulfur compound during photolysis, see J. Guttenplan and S.G. Cohen, Chem. Commun., 247 (1969).

11. In eq 14, k_{12} is omitted since $k_{13} \gg k_{12}$.

12. (a) The rate constant for hydrogen atom addition to benzene in solution is $\sim 10^{9}$ l./(mol-sec),[12b,13] whereas that for hydrogen abstraction by the H-atom from organic hydrogen donors is 10^{6}-10^{8} l./(mol-sec);[7] (b) M.C. Sauer, Jr., and B. Ward, J. Phys. Chem., 71, 3971 (1967).

13. The rate constant for the addition of the H-atoms to benzene in the gas phase is about 10^7 1/(mol-sec); see K. Yang, J. Amer. Chem. Soc., 84, 3795 (1962).

14. Similar work has been done in polymerizations in which chain transfer constants of alcohol vs. alcohol-d were determined; see M. Morton, J.A. Cala and I. Piirma, ibid., 78, 5394 (1956).

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21. Hydrogen abstraction by electronically excited alkene has been reported; see H.M. Rosenberg and P. Serve, ibid., 92, 4746 (1970).

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23. (a) It is perhaps surprising that the relative reactivity of benzene is so high in this system, since it is almost inert to hydrogen abstraction in other radical reactions;[24] see J.H. Bell and H. Linschitz, ibid., 85, 528 (1963); F.G. Edwards and F.R. Mayo, ibid., 72, 1265 (1950); A.L. Williams, E. Oberright and J.B. Brooks, ibid., 78, 1190 (1956); C. Walling and B. Jacknow, ibid., 82, 6108 (1960); reference 22; on the other hand,

G. Henrici-Olive and S. Olive (Fortschr. Hochpolym.-Forsch., 2, 496 (1961)) report that the transfer constant for benzene in the polymerization of styrene is nearly 40% that of toluene; (b) C. Walling, "Free Radicals in Solution," Wiley, New York, 1957, p 491ff; (c) see also reference 12b, and references cited therein.

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32. See reference 5, p 150ff.

VITA

Richard Wayne Henderson was born in Baton Rouge, Louisiana on November 6, 1943. He graduated from Baton Rouge High School in May of 1961. He entered Louisiana State University in September of 1961 and received the Bachelor of Science degree in Chemistry in May of 1966. He entered the Graduate School of Louisiana State University in June of 1966, and was awarded a Traineeship by the National Aeronautics and Space Administration and subsequently a Research Assistantship by the National Institutes of Health.

He married the former Caroline Jerlyn Smith on July 2, 1966, and his son, Brian Robert, was born on March 7, 1971. He is a member of the American Chemical Society, Phi Kappa Phi, and Phi Lambda Upsilon.

He is currently a candidate for the degree of Doctor of Philosophy at Louisiana State University.

EXAMINATION AND THESIS REPORT

Candidate: Richard Wayne Henderson

Major Field: Chemistry

Title of Thesis: Reactions of Radicals. Part I. Use of Hydrogen Isotopes in Polymer Chemistry. Part II. Hydrogen Atom Reactions in Solution.

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

March 15, 1971